SOME APPLICATIONS OF FLUCTUATION SOLUTION THEORY
TO MULTIPHASE SYSTEMS OF NONELECTROLYTES

BY

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KEY TO SYMBOLS

a_i = activity of component i

A = Helmholtz free energy, 2-suffix Margules equation constant, constant

B = constant

c = molecular direct correlation function

C = direct correlation function integral, constant

D = constant

f = fugacity

G = Gibbs free energy

g = radial distribution function

h = total correlation function

H = enthalpy, Hamiltonian

H_{ij} = Henry's constant of solute i in pure solvent j

k = Boltzmann constant

k_{ij} = binary parameter

n = number of components

N_i = number of molecules of component i

p = conjugate momentum, probability density

P = pressure, probability

q = generalized coordinate

Q = Canonical partition function

$\underline{r}$ = position vector

R	=	gas constant
S	=	entropy
T	=	temperature, kinetic energy
V	=	volume
x_i	=	liquid mole fraction of component i
y_i	=	vapor mole fraction of component i
z	=	compressibility factor
Z	=	some general thermodynamic property
α	=	adjustable parameter
β	=	binary parameter
γ	=	nonsphericity parameter
γ_i	=	activity coefficient of component i
δ_{ij}	=	Kronecker delta
ε	=	energy parameter in intermolecular potential function
η	=	packing fraction
κ	=	isothermal compressibility
λ	=	constant
μ_i	=	chemical potential of component i
ξ_i	=	$\frac{\pi}{6}\rho\sigma^i$
Ξ	=	grand canonical partition function
ρ	=	number density, molar density
σ	=	hard sphere diameter
ϕ_i	=	volume fraction of component i
$\underline{\Omega}$	=	vector of Euler angles

Subscripts

c	=	critical property
i,j, . . .	=	components
ij	=	pair of components
s	=	angle average

Superscripts

calc	=	calculated property
E	=	excess property
f	=	final state
hs	=	hard sphere property
id	=	ideal property
L	=	liquid phase
r	=	reference state
V	=	vapor phase
∞	=	infinite dilution
*	=	characteristic parameter

Special Symbols

— (as in $\underline{A}$)	vector or matrix quantity
— (as in $\overline{V}_i$)	partial molar property
~ (as in $\tilde{\rho}$)	reduced property
o (as in v_i^o)	pure component property
< > (as in $\langle N_i \rangle$)	ensemble average

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Engineering design requires increasing accuracy in the quantitative description of the thermodynamic properties of fluid mixtures. To meet this demand, present methods of property calculations are more theoretical than empirical; they relate microscopic behavior and intermolecular potentials to macroscopic properties using statistical mechanical formulations. Fluctuation solution theory expresses the solution compressibility and component molar volumes and activity coefficients in terms of integrals of the direct correlation function. These are independent of pairwise additivity and generally insensitive to the details of the intermolecular forces.

The present work applies this theory to gas solubility in mixed solvents and to liquid-liquid equilibria. It includes an extensive collection of experimental direct

correlation function integrals for liquids and makes some suggestions for improving the original model. In particular, ideal solution direct correlation function integrals have a simple relation to composition. In nonideal mixtures, while the form may appear more complex, simple relations are also consistent with the data.

It has been found that the fluctuation solution form of the Van der Waals model describes liquid-liquid equilibria in binary systems as well as any other liquid model currently in use. It is also excellent for gases in mixed solvents. However, its use of only one parameter is a severe handicap when the model is applied to multicomponent liquid-liquid systems. To improve the situation, different alternatives have been examined but none has proven entirely satisfactory. Various choices of hard sphere expression in the perturbed hard sphere model leads to the same inadequate results in mixtures. Hard convex body equations make no improvement. The major problem is indicated by the fact that at infinite dilution in a binary system the model does not account for the reality of the unlike interactions. The introduction of a quadratic term in density may be a way to solve this problem. A study of gases in mixed solvents is also included.

CHAPTER 1
INTRODUCTION

Design of chemical processing equipments requires
accurate phase equilibria descriptions. To cover all
necessary ranges of conditions would demand a large amount
of experimental work. A way to avoid the expensive and the
time-consuming path of experiments is to predict the behav-
ior from a minimum of fundamental data, e.g., multicompo-
nent system properties from pure component and binary
properties.

Different classes of fluid phase equilibria arise from
the physical and chemical nature of the mixture. Thus, it
is possible to talk about two or more phases among gases,
liquids, and solids including multifluid systems. The sub-
stances can be categorized as electrolytes and nonelectro-
lytes with important subdivisions of nonpolar, polar, and
aqueous solutions of discrete or continuous, and small or
polymeric molecules. Further characterization and division
are possible using the conditions of temperature and pres-
sure on the mixture. This work is an attempt to build a
predictive method for liquid-liquid equilibria of nonelec-
trolyte systems of nonpolymeric molecules.

Thermodynamics tells us that at two-phase equilibrium
the chemical potential of each component is the same in

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both phases. These chemical potentials depend on thermo-dynamic variables of the system such as temperature, pressure, volume, and chemical composition. The problem is to find a good relation to expression for the chemical potential in terms of these variables. In order to simplify the problem, it is common to introduce functions such as the fugacity and activity (Prausnitz, 1969). Hence, the phase equilibria problem reduces to finding a model for the fugacity or the activity.

The usual predictive methods in liquid-liquid phase equilibria can be divided in two classes: those that use the same equation for both phases and those that use different equations for each phase. The first class works with fugacity coefficients and writes them from a P-v-T-x equation of state. The second class works with activities or activity coefficients in the liquid phase and writes them from excess Gibbs energy expressions.

The fluctuation solution theory approach used here does not belong to either of these two classes. It employs for the liquid phase an equation of state only for the liquid phase rather than both gas and liquid as the first class does, and it is not derived from an excess Gibbs energy model. Another distinctive and important point is the generality of the approach where expressions for the species, whether gases, liquids, or ions, are evaluated in the same way.

In the fluctuation solution theory, thermodynamic properties are obtained by integration of a model for derivatives of the properties so the approach is likely to be less sensitive to errors in modelling. In addition, the theory employs temperature and component density as independent variables, as opposed to pressure, temperature and mole fraction which are normally the choice. This allows the possibility of simpler expressions since, as will be shown, the results are more sensitive to the density.

The goal in this work is to build on the success of the one-parameter corresponding states model for pure component liquids of Brelvi (1973) and the two-parameter corresponding states model for solutions containing supercritical components of Mathias (1978). Other related work has dealt with solutions of "reactive components" including electrolytes (Perry, 1980) and groups (Telotte and O'Connell, 1982).

Chapter 2 describes the fluctuation solution theory and how it can be used to solve phase equilibrium problems. Using the grand canonical ensemble, direct correlation function integrals (DCFI) are related to the concentration derivatives of the chemical potentials of the components. When these expressions are integrated, equations for the thermodynamic properties of interest are obtained. The chapter ends with the stability conditions for multicomponent systems in this new theory.

Chapter 3 displays direct correlation function integrals for many ideal and nonideal binary systems. These integrals are obtained from volumetric and excess Gibbs energy correlation of measured data, so these integrals are considered to be experimental. The apparent composition dependence in some cases is more complex than expected. However, it is shown that a simpler form of the DCFI produces essentially the same property results. This indicates the direction of sensitivity for DCFI modelling of thermodynamic properties.

Chapter 4 presents a model for direct correlation function integrals. Mathias (1978) used it to describe the solubility of gases in liquids. The model writes the DCFI in the Van der Waals form, a hard sphere expression plus a correction term linear in the density. In this chapter, we analyze two modifications to this model. One of them introduces a parameter in the hard sphere equation. The correction term is adjusted to make the model accurately describe pure component properties. The other replaces the hard sphere equation by a hard convex body expression. Finally, we show application of the Mathias model to the solubility of gases in binary solvents.

Chapter 5 describes application of the model of Chapter 4 to liquid-liquid equilibria. This is a more severe test to the fluctuation solution theory because the temperature effects and the balance of like and unlike attractive forces are more important here than in gas-liquid

equilibria. As given, the model is limited to one binary parameter. As a result, the correlation of ternary systems is poor. Different ways are tried to use two binary parameters.

Chapter 6 suggests a more drastic modification to the model than in Chapter 5. First, we analyze the effectiveness of the hard sphere mixture expressions as a reference for describing direct correlation function integrals. Then, we address the problem of the infinite dilution behavior of the direct correlation function integrals which in binary systems depend on the interaction between the components. Finally, we look at expressions for the direct correlation function integrals that are obtained from some common excess Gibbs energy models.

CHAPTER 2
THERMODYNAMICS AND FLUCTUATION SOLUTION THEORY

2.1 Introduction

This chapter describes fluctuation solution theory and
how it may be employed for solving phase equilibria problems.

Section 2.2 employs the grand canonical ensemble in two
ways: first, to relate composition fluctuations to deriva-
tives of the chemical potential of the components, and
second, to relate the composition fluctuations to integrals
of the pair distribution function of the molecular pairs
present in a solution. When the composition fluctuations
are eliminated, direct correlation function integrals are
related to the derivatives of the basic equilibria equa-
tions. Section 2.3 shows how these quantities are related
to the thermodynamic properties of interest. Section 2.4
shows how stability conditions are easily evaluated in the
new theory.

Before going into the details of the derivation, we
note the two most desirable features of the theory.

1. Thermodynamic properties are obtained by integra-
tion of a simple model instead of the normal situation that
requires a derivative of a complex expression. Numerical
analysis indicates that the present approach is less sen-
sitive to errors in modelling.

2. The fluctuation solution theory employs temperature and component density (component number density at microscopic level) as independent variables. From a statistical mechanical point of view, this set is the most appropriate for theoretical work. In contrast, pressure, temperature, and mole fraction are the standard choice in thermodynamics, but their use causes difficulty in developing a complete equation of state for either the fluid phases or the liquid alone.

2.2 Statistical Thermodynamics

The basic references for this chapter are Kirkwood and Buff (1951), O'Connell (1971a), and Rowlinson and Swinton (1982). The interactions which determine the bulk properties of the matter are electromagnetic; they arise from the Coulomb interactions between nuclei and electrons. One way to predict the properties of liquid would be to solve the many body Schrödinger equation describing the motion of the nuclei and electrons. To facilitate the task there are three basic simplifications.

The first is the Born-Oppenheimer approximation for a static configuration of the nuclei relative to the electronic motion.

The second approximation is to neglect any coupling between vibrational and center of mass motions of the molecule. For complex molecules this means that they are rigid. The position and orientation of a rigid molecule i are

defined by six coordinates, the center of mass coordinates $\underline{r}_i$ and the Euler angles $\underline{\Omega}_i$; in the case of axially symmetric molecules, two angles are sufficient to define the orientation. As the intermolecular forces are dependent both on position and orientation, we shall denote the potential energy function of N molecules by the symbol $U_N(\underline{r}^N, \underline{\Omega}^N)$.

The third approximation is that we can use classical mechanics and classical statistical mechanics in describing the behavior of the molecules.

We consider an open region of volume V, which is a part of a system of infinite extent, and we select the grand canonical ensemble which is the most convenient for deriving theoretical results to represent its statistical behavior. The volume contains exactly $N_1, N_2, \ldots, N_n$ molecules of the n-species of the multicomponent system. The system is defined by the variables temperature (T), total volume (V), and chemical potential of the n components $(\underline{\mu})$. We can write the probability that the n-component system will contain $N_1, N_2 \ldots N_n$ molecules of the n species as

$$P_{(N_1, N_2, \ldots N_n)} = \frac{\exp\left(\frac{1}{kT} \sum_{1}^{n} N_i \mu_i\right) Q(T, V, N_1, \ldots, N_n)}{\Xi} \quad (2-1)$$

where k is the Boltzmann constant; Q and Ξ are the canonical and grand canonical partition functions defined by

$$Q = \int \ldots \int e^{-H/kT} dp^N dq^N \quad (2-2)$$

with H as the hamiltonian of total energy of the system or
the result of adding the kinetic energy function T to the
potential energy function U_N.

$$\Xi = \sum_{N_1 \ldots N_n} e^{+ \frac{1}{kT} \sum_1^n N_i \mu_i} Q \qquad (2-3)$$

From the definition of the average number of molecules
we can write

$$\langle N_i \rangle = \sum_{N_1 \ldots N_n} N_i P$$

$$= \frac{kT}{\Xi} \frac{\partial \Xi}{\partial \mu_i} \Bigg|_{T,V,\mu_{j \neq 1}} \qquad (2-4)$$

From the definition of the average number of pairs of mole-
cules we can write

$$\langle N_i N_j \rangle = \sum_{N_1 \ldots N_n} N_i N_j P$$

$$= \frac{(kT)^2}{\Xi} \frac{\partial^2 \Xi}{\partial \mu_i \partial \mu_j}$$

$$= \langle N_i \rangle \langle N_j \rangle + \frac{\partial \langle N_i \rangle}{\partial \mu_j / kT} \Bigg|_{T,V,\mu_{k \neq j}} \qquad (2-5)$$

Distribution functions allow a complete description of
the microscopic structure of liquids and give a quantitative
measure of the correlations between the positions of

different particles. The most important distribution func-
tions are the singlet and pair molecular functions.

For a pure fluid, the probability density p that M
particular molecules lie in the elements $d\underline{r}_1$, $d\underline{\Omega}_1$; $d\underline{r}_2$,
$d\underline{\Omega}_2$; ...; $d\underline{r}_M$, $d\underline{\Omega}_M$ is given by

$$p = \sum_{N=0}^{\infty} \frac{\exp (N\beta\mu)}{N! \ \Xi} \int ... \int \ \exp (-\beta U_N)$$

$$d\underline{r}_{M+1} \ d\underline{\Omega}_{M+1} \cdots d\underline{r}_N \ d\underline{\Omega}_N \qquad (2-6)$$

There are $N(N-1)...(N-M+1)$ different sets of molecules which
can occupy the volume elements so that the total probability
density that any N molecules occupy these elements is given
by

$$n^{(M)} (\underline{r}_1,\underline{\Omega}_1;...; \ \underline{r}_M,\underline{\Omega}_M) = \rho^M g^{(M)} (\underline{r}_1,\underline{\Omega}_1;...; \ \underline{r}_M,\underline{\Omega}_M)$$

$$= N! \ \frac{p}{(N-M)!} \qquad (2-7)$$

The functions $n^{(M)}$ and $g^{(M)}$ are called M-molecular dis-
tribution functions. For an isotropic fluid, $n^{(1)}$ is just
the number density and will depend only on the distance
$r_{12} = |\underline{r}_1 - \underline{r}_2|$, its direction and the orientations of the
molecules with respect to each other. The pair distribu-
tion $g^{(2)} (\underline{r}_1,\underline{\Omega}_1,\underline{r}_2,\underline{\Omega}_2)$ plays an important role in the theory
of liquids. It goes to unity as the distance between the
molecules becomes large, indicating that no correlation

exists. For spherical molecules the pair distribution depends on the distance only, and it is called the radial distribution function. For nonspherical molecules we define the radial distribution function by

$$g_s(r_{12}) = \iint g(r_{12},\underline{\Omega}_1,\underline{\Omega}_2)\,d\underline{\Omega}_1 d\underline{\Omega}_2 \qquad (2\text{-}8)$$

In equation (2-8) the subscript s indicates an angle average.

Other important functions are the total correlation function, $h \equiv g-1$, and the direct correlation function, c, defined by the Ornstein-Zernike equation for a pure homogeneous fluid.

$$h(\underline{r}_1,\underline{\Omega}_1,\underline{r}_2,\underline{\Omega}_2) = c(\underline{r}_1,\underline{\Omega}_1,\underline{r}_2,\underline{\Omega}_2)$$

$$+ \rho \int h(\underline{r}_1,\underline{r}_3,\underline{\Omega}_1,\underline{\Omega}_3)\ c(\underline{r}_2,\underline{r}_3,\underline{\Omega}_2,\underline{\Omega}_3)\ d\underline{r}_3 d\underline{\Omega}_3 \qquad (2\text{-}9)$$

(The superscript 2 that above had indicated a pair molecular function has now been dropped.) We can write the angle averaged version as

$$h_s(r_{12}) = c_s(r_{12}) + \rho \int h_s(r_{13})c_s(r_{23})d\underline{r}_3 \qquad (2\text{-}10)$$

Figure (2-1) compares the range and shape of the pair potential, the radial distribution function, and the direct correlation function of a spherically symmetric molecule.
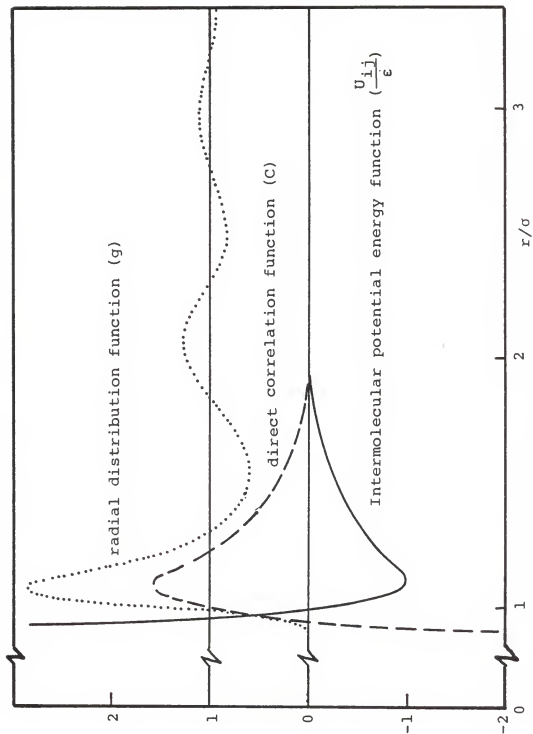
Figure 2-1. Correlation functions for spherically symmetric molecules.

For a system of n components, we define functions consistent with those for pure fluids, the single molecular distribution function, $n_i^{(1)}(\underline{r}_1)$ as the time-averaged density of molecules of type i at the position $\underline{r}_1$. The pair molecular distribution function, $n_{ij}^{(2)}(\underline{r}_1,\underline{r}_2)$, is defined as the average density of molecular pairs of type i at $\underline{r}_1$ and type j at $\underline{r}_2$. Integration of the above distribution functions over the volume of the system gives, with the subscript s eliminated,

$$\int n_i^{(1)}(\underline{r}_1)d\underline{r}_1 = <N_i> \qquad (2\text{-}11)$$

$$\int\int n_{ij}^{(2)}(\underline{r}_1,\underline{r}_2)d\underline{r}_1\,d\underline{r}_2 = <N_iN_j> - \delta_{ij}<N_i> \qquad (2\text{-}12)$$

The radial distribution function is defined by

$$g_{ij}^{(2)}(\underline{r}_1,\underline{r}_2) = \frac{n_{ij}^{(2)}(\underline{r}_1,\underline{r}_2)}{n_i^{(1)}(\underline{r}_1)n_j^{(1)}(\underline{r}_2)}$$

$$= g_{ij}(\underline{r}_1,\underline{r}_2) \qquad (2\text{-}13)$$

Using this radial distribution function in equation (2-12), we can write

$$\frac{1}{V}\int (g_{ij}(r_{12})-1)\ dr = \frac{<N_iN_j> - <N_i><N_j>}{<N_i><N_j>} - \frac{\delta_{ij}}{<N_i>} \qquad (2\text{-}14)$$

Combining equations (2-5) and (2-14) we get

$$\frac{1}{<N_i>} \frac{\partial <N_i>}{\partial \mu_j/kT} \Bigg|_{T,V,\mu_{k \neq j}} = \rho_j \int (g_{ij}(r_{12})-1) \, d\underline{r}_2 + \delta_{ij} \quad (2-15)$$

As the volume of the ensemble is constant, the above equation can be written

$$\frac{1}{\rho} \frac{\partial \rho_i}{\partial \mu_j/kT} \Bigg|_{T,V,\mu_{k \neq j}} = x_i x_j \rho \int (g_{ij}(r_{12})-1) \, d\underline{r}_2$$

$$+ x_i \, \delta_{ij} \quad (2-16)$$

It is possible to work with equation (2-16) in developing models for liquid solutions, but the approach leads to complex equations which are ill-defined at the critical point. Therefore, it is desirable to express equation (2-16) in terms of the direct correlation function which has the same range as the intermolecular potential function. Besides, there are strong indications that the direct correlation functions are less difficult to model (Gubbins and O'Connell, 1974). For a system of n-components the equivalent equation to (2-10) is

$$h_{ij}(r_{12}) = g_{ij}(r_{12}) - 1$$

$$= c_{ij}(r_{12}) + \sum_{k=1}^{n} \rho_k \int c_{ik}(r_{13}) h_{jk}(r_{23}) d\underline{r}_3 \quad (2-17)$$

We must emphasize that in equation (2-17) we have dropped the subscript s that indicates an angle average and the

superscript (2) that indicates that they are pair molecular functions. Integrating equation (2-17) over all $\underline{r}_2$ gives

$$\rho \int h_{ij}(r_{12})d\underline{r}_2 = \rho \int c_{ij}(r_{12})dr_2$$

$$+ \sum_1^n x_k \rho^2 \int\int c_{ik}(r_{13})h_{jk}(r_{23})d\underline{r}_3 d\underline{r}_2 \tag{2-18}$$

In matrix notation equation (2-18) can be written as

$$\underline{H} = \underline{C} + \underline{C}\ \underline{X}\ \underline{H} \tag{2-19}$$

where $\underline{C}$ is a matrix of direct correlation function integrals C_{ij}. The term $\underline{H}$ is a matrix with total correlation function integrals, H_{ij}; $\underline{X}$ is a diagonal matrix with elements X_{ii} equal to the mol fraction x_i. Postmultiplying equation (2-19) by the matrix $\underline{X}$ and adding $\underline{I}$

$$\underline{I} + \underline{H}\ \underline{X} = \underline{C}\ \underline{X}\ +\ \underline{C}\ \underline{X}\ \underline{H}\ \underline{X}\ +\ \underline{I} \tag{2-20}$$

Equation (2-20) can also be rearranged to give

$$(\underline{I}\ =\ \underline{H}\ \underline{X})\ (\underline{I}\ -\ \underline{C}\ \underline{X})\ =\ \underline{I} \tag{2-21}$$

We can write equation (2-16) in matrix form as

$$\underline{D}\ +\ \underline{X}\ (\underline{I}\ +\ \underline{H}\ \underline{X}) \tag{2-16a}$$

where the elements of $\underline{D}$ are the left-hand sides of equation (2-16).

Combining equations (2-16a) and 2-21), we get

$$\underline{D}^{-1} = (\underline{x}^{-1} - \underline{C}) \qquad (2-22)$$

After dividing by ρ, each element of the matrix equation (2-22) is

$$\frac{N}{\rho} \left. \frac{\partial \mu_i / kT}{\partial N_j} \right|_{T,V,N_{k \neq j}} = \left. \frac{\partial \mu_i / kT}{\partial \rho_j} \right|_{T,\rho_{k \neq j}}$$

$$= \frac{\delta_{ij}}{\rho_i} - \frac{C_{ij}}{\rho} \qquad (2-23)$$

The Gibbs-Duhem equation at constant temperature relates changes in pressure and chemical potential as

$$VdP = \sum_1^n N_i d\mu_i \qquad (2-24)$$

Dividing equation (2-24) by $d\rho_j$ at fixed T and $\rho_{k \neq j}$ gives

$$\left. \frac{\partial P / kT}{\partial \rho_j} \right|_{T,\rho_{k \neq j}} = \sum_1^n \rho_i \left. \frac{\partial \mu_i / kT}{\partial \rho_j} \right|_{T,\rho_{k \neq j}} \qquad (2-25)$$

Finally, using equation (2-23) in equation (2-25) we get

$$\frac{N}{\rho} \left. \frac{\partial P/kT}{\partial N_j} \right|_{T,V,N_{k \neq j}} = \left. \frac{\partial P/kT}{\partial \rho_j} \right|_{T,\rho_{k \neq j}}$$

$$= \sum_{1}^{n} x_i \, (1 - C_{ij}) \qquad (2-26)$$

where x_i is given by

$$x_i = \frac{\rho_i}{\rho}$$

Equations (2-23) and (2-26) are the basic equations of the fluctuation solution theory when T and ρ are the independent intensive variables of the system.

2.3 Thermodynamics

Prior to using the basic equations it must be recognized that

a) The most common approach in modelling thermodynamic properties of solutions requires taking derivatives of the system free energy. On the contrary, here we are going to use the integrals of a model for the direct correlation function integrals. In general this is expected to produce results that are less sensitive to the model approximation.

b) The most common representation of thermodynamic properties uses temperature, pressure, and mole fraction of the components of the system as the independent variables. But equations (2-23) and (2-26) use temperature and

concentration of the components. This means that in solving the system of equations the pressure equation (equation (2-26)) must be used to find the density of the solution, ρ (O'Connell, 1981).

The isothermal differential of any thermodynamic property Z, which is a function of temperature and component density, is given by

$$dZ = \sum_{1}^{n} \frac{\partial Z}{\partial \rho_i} \Bigg|_{T,\rho_{j \neq i}} d\rho_i \tag{2-27}$$

Thus, the isothermal change in the thermodynamic property Z from an initial state r to a final state f is

$$Z^f - Z^r = \sum_{i} \int_{\rho_i^r}^{\rho_i^f} \frac{\partial Z}{\partial \rho_i} \Bigg|_{T,\rho_{j \neq i}} d\rho_i \tag{2-28}$$

Then for the change in pressure, using equation (2-26), we obtain

$$\frac{P^f - P^r}{RT} = (\rho^f - \rho^r) - \sum_{i} \int_{\rho_i^r}^{\rho_i^f} \sum_{j} \frac{\rho_i C_{ij}(T,\underline{\rho})}{\rho} \Bigg|_{T,\rho_{j \neq i}} d\rho_i \tag{2-29}$$

And for the change in chemical potentials, using equations (2-23), we get

$$\frac{\mu_i^f - \mu_i^r}{RT} = \ln \frac{\rho_i^f}{\rho_i^r} - \sum_{j} \int_{\rho_j^r}^{\rho_j^f} \frac{C_{ij}}{\rho} \Bigg|_{T,\rho_{k \neq j}} d\rho_j \tag{2-30}$$

In solving phase equilibrium problems it is more convenient to work with the fugacity or activity coefficient than with chemical potential. As

$$\mu_{i(T,\underline{\rho})} = \mu_i^0(T,\underline{\rho}^r) + RT \ln \gamma_i(T,\underline{\rho}) \, x_i \qquad (2\text{-}31a)$$

$$= \mu_i^0(T,\underline{\rho}^r) + RT \ln \frac{f_i(T,\underline{\rho})}{f_i^r(T,\underline{\rho}^r)} \qquad (2\text{-}31b)$$

We can rewrite equations (2-31a) and (2-31b)

$$\left. \frac{\partial \ln \gamma_i}{\partial \rho_j} \right|_{T,\rho_{k \neq j}} = \frac{(1 - C_{ij})}{\rho} \qquad (2\text{-}32)$$

$$\left. \frac{\partial \ln f_i}{\partial \rho_j} \right|_{T,\rho_{k \neq j}} = \frac{\delta_{ij}}{\rho_i} - \frac{C_{ij}}{\rho} \qquad (2\text{-}33)$$

Thus for the change in fugacity we get

$$\ln f_i^f - \ln f_i^r = \ln \frac{\rho_i^f}{\rho_i^r} - \sum_j \int_{\rho_j^r}^{\rho_j^f} \frac{C_{ij}(T,\underline{\rho})}{\rho} \, d\rho_j \qquad (2\text{-}34)$$

And for the change in activity coefficient we set

$$\ln \gamma_i^f - \ln \gamma_i^r = \sum_j \int_{\rho_j^r}^{\rho_j^f} [\, 1 - \frac{C_{ij}(T,\underline{\rho})}{\rho} \,] d\rho_j \qquad (2\text{-}35)$$

In summary, the procedure for finding pressure and chemical potentials (or their equivalent properties, fugacities, or activity coefficients) requires three steps:

1) Choose an appropriate lower integration limit or reference state for the set of partial differential equations.

2) Solve iteratively equation (2-29) for the final total density.

3) Calculate the activity coefficient for component i using equation (2-35).

2.4 Applications to Phase Equilibria Problems

The thermodynamic equilibrium between m different phases in an n multicomponent system is given by

$$\mu_i^1 = \mu_i^2 = \ldots = \mu_i^m \qquad i = 1, \ldots, n \quad (2-36)$$

where μ_i^j is the chemical potential of component i in phase j. As equation (2-36) is not very useful in the modeling real systems, it is convenient to replace it by an expression that uses the fugacity as defined by

$$\mu_i = \mu_i^o + RT \ln \frac{f_i}{f_i^o} \qquad (2-37)$$

where f_i is the fugacity of component i and the superscript o indicates the reference for measuring the thermodynamic

properties. The reference states are chosen different for each phase. The only assumption is that these reference states are at the same temperature. Then, using equation (2-37) in equation (2-36), the equilibria between phases could be described by

$$f_i^1 = f_i^2 = \ldots = f_i^m \quad i = 1, \ldots, n \quad (2\text{-}38)$$

Another possibility is working with the activity as defined as

$$a_i = \frac{f_i}{f_i^o} \quad (2\text{-}39)$$

or

$$\mu_i = \mu_i^o + RT \ln a_i \quad (2\text{-}40)$$

We can rewrite equation (2-38) in terms of the activities a_i

$$f_i^{o1} a_i^1 = f_i^{o2} a_i^2 = \ldots$$

$$= f_i^{om} a_i^m \quad i = 1, \ldots, n \quad (2\text{-}41)$$

Another alternative is to introduce the activity coefficient defined by

$$a_i = \gamma_i x_i \qquad (2\text{-}42)$$

With this last definition equation (2-38) can be written as

$$f_i^{o1} \gamma_i^1 x_i^1 = f_i^{o2} \gamma_i^2 x_i^2 = \ldots$$

$$= f_i^{om} \gamma_i^m x_i^m \qquad i = i, \ldots, n \qquad (2\text{-}43)$$

where the superscript o indicates the reference state, the superscript j the phase, and the subscript i the component. Up to this point we have presented the basic equations without any reference to two basic problems, the reference state and the variables of which the properties depend upon.

The standard choice is to adopt a reference state that is composition independent. An ideal solution is defined as the basis for real solutions

$$\mu_i^{id} = \mu_i^o(T,P) + RT \ln x_i \qquad (2\text{-}44a)$$

or

$$f_i^{id} = x_i f_i^o \qquad (2\text{-}44b)$$

where we have chosen the variables temperature, pressure, and mole fraction to describe the thermodynamic properties.

It is found experimentally that all dilute solutions, where the mole fractions of one component are near zero,

behave like ideal solutions. These ideal mixtures follow Henry's law. On the other hand, there are solutions that behave ideally near the pure component composition. These mixtures follow Raoult's law. Deviations from ideal solution are contained in the activity coefficient.

For the particular case of the solubility of gases in liquids, equation (2-38) for component i takes the following form:

$$f_i^V(T,P,\underline{y}) \;=\; f_i^L(T,P,\underline{x}) \tag{2-45}$$

where we have chosen temperature, pressure, and mole fraction as variables, $\underline{y}$ being the set of vapor mole fractions and $\underline{x}$ being the set of liquid mole fractions.

The fugacity of the liquid phase can be expressed in several alternatives; the more important ones are

$$f_i^L \;=\; x_i \; \phi_i(T,P,\underline{x}) \, P \tag{2-46}$$

$$\;=\; x_i \; \gamma_i(T,\underline{x}) \; f_i^O(T) \; \exp\left[\int_{P_i^O}^{P} \left. \frac{\overline{v}_i(T,P,\underline{x})}{RT} \right|_{T,\underline{x}} dP \right] \tag{2-47}$$

$$\;=\; x_i \; \gamma_i(T,P,\underline{x}) \; f_i^O(T) \tag{2-48}$$

Equation (2-46) is used when an equation of state is available to describe both phases. Equations (2-47) and

(2-48) can be written from equation (2-43). In equation (2-47) the exponential term is the Poynting correction. Equation (2-48) is more appropriate for working with the equations written in section 2.3, where equation (2-35) provides the activity coefficient necessary for equation (2-48). The dependence of γ_i in equation (2-48) can be taken as either $(T,P,\underline{x})$ or as (T,ρ), the latter being the natural variables for fluctuation solution theory.

For the particular case of the liquid immiscibility, equation (2-38) for component i takes the following form:

$$f_i' \ (T,P,\underline{x}') \ = \ f_i'' \ (T,P,\underline{x}'') \qquad (2-49)$$

where we have again chosen temperature, pressure, and mole fraction as variables, $\underline{x}$ is the set of liquid mole fractions, and the superscripts ' and " indicate two different liquid phases. If the same reference state is chosen for both phases, equation (2-49) can be written as

$$\gamma_i' \ (T,P,\underline{x}') \ x_i' \ = \ \gamma_i'' \ (T,P,\underline{x}'') \ x_i'' \qquad (2-50)$$

Equation (2-50) can be used with equation (2-35) of section 2.3.

Comparison of equations (2-50) and (2-45) shows why the problem of liquid-liquid equilibria is more difficult. First, there is no independent determination of the component fugacity as in the vapor-liquid case with the

vapor fugacity. The same fact does not allow us to check the consistency of data. Second, pure component fugacity values have no influence, and all variations arise from nonideality, expressed by the activity coefficient. This increases sensitivity of the results to the model.

Equation (2-36) and the others derived from it say nothing about equilibrium stability. Any thermodynamic density variable (entropy, internal energy, Helmholtz free energy, etc.) may be employed to express stability criteria. The Helmholtz free energy is chosen here primarily because its natural variables agree with variables in which direct correlation function integrals are written. We can state that a system is in a stable equilibrium state at constant volume, temperature, and number of moles when its Helmholtz free energy is at a minimum. Or, in other words, at equilibrium any small perturbation at fixed $T, V, \underline{N}$ results in an increase in the total Helmholtz free energy. For such small perturbation, A can be expanded in a Taylor series

$$\Delta A = \delta A + \delta^2 A + \delta^3 A + \ldots > 0 \qquad (2\text{-}51a)$$

For equilibrium to exist,

$$\delta A = 0$$

and for the system to be stable,

$$\delta^j A > 0$$

where j is the first nonvanishing variation. Choosing $j = 2$,

$$\delta^2 A > 0 \tag{2-52}$$

We mentally divide the system in two subsystems, one of them very small. We generate a perturbation by allowing a virtual transfer of volume and masses across the hypothetical surface separating the two subsystems. As one of the subsystems is very small and both are at equilibrium, equation (2-51a) transforms to

$$\Delta A = \delta A^2$$
$$= N \, d^2 a > 0 \tag{2-51b}$$

where a is the molar free Helmoltz energy (small letters represent molar properties).

For convenience we prefer to work with extensive properties. Introducing the total number of moles inside $d^2 a$, we get the second differential of the free Helmoltz energy which depends, here, on volume and (n-1) number of moles (Modell and Reid, 1983), where

$$d^2 A = \underline{P}^T \, \underline{D} \, \underline{P} \tag{2-53}$$

where

$$\underline{P} = \begin{bmatrix} dV \\ dN_1 \\ \vdots \\ dN_{n-1} \end{bmatrix} \qquad (2-54)$$

$$\underline{D} = \begin{bmatrix} \dfrac{\partial^2 A}{\partial V^2} & \cdots & \dfrac{\partial^2 A}{\partial N_{n-1} \partial V} \\ \vdots & & \\ \dfrac{\partial^2 A}{\partial V \partial N_{n-1}} & \cdots & \dfrac{\partial^2 A}{\partial N_{n-1} \partial N_{n-1}} \end{bmatrix} \qquad (2-55)$$

The stability criteria are the criteria for the quadratic given by equation (2-53) to be positive definite. The quadratic will assume positive values for any variation in $\underline{P}$ if and only if the determinant of $\underline{D}$ given by equation (2-55) and all its principal minors are greater than zero. For symmetric matrices, the first positive definite condition to break is the determinant condition. Hence, the spinodal is defined as that locus of points satisfying det $\underline{D} = 0$.

For the pure component case, the matrix in equation (2-55) has only one element and the stability criterion derived from it is

$$\left. \frac{\partial^2 A}{\partial V^2} \right|_T > 0 \qquad \text{or} \qquad \kappa > 0 \qquad (2-56)$$

Equation (2-56) is the mechanical stability criterion. There is also a thermal stability criterion, but it cannot

be derived using the Helmholtz free energy representation.
From the internal energy representation we find that

$$\frac{\partial^2 U}{\partial S^2}\bigg|_V > 0 \qquad \text{or} \qquad C_v > 0 \qquad (2\text{-}57)$$

Equations (2-56) and (2-57) are the classical stability criteria whose physical content is known as the Le Châtelier principle. According to this principle, the criterion for stability is that all spontaneous processes induced by any deviation from equilibrium will be in the direction of restoring the system to equilibrium.

For the case of a binary mixture the positive definite condition for the matrix equation (2-55) is

$$\begin{vmatrix} \dfrac{\partial^2 A}{\partial V^2} & \dfrac{\partial^2 A}{\partial N_1 \partial V} \\[2ex] \dfrac{\partial^2 A}{\partial V \partial N_1} & \dfrac{\partial^2 A}{\partial N_1^2} \end{vmatrix} > 0 \qquad (2\text{-}58)$$

with all its principal minors greater than zero.

Now, it is possible to link the condition given by equation (2-58) with the equations given by the fluctuation theory. Using equations (2-23) and (2-26) we get for the elements of the determinant in equation (2-58)

$$\frac{\partial^2 A}{\partial V^2}\bigg|_{T,\underline{N}} = -\frac{\partial P}{\partial V}\bigg|_{T,\underline{N}}$$

$$= \frac{1}{V \kappa}$$

$$= \frac{\rho RT}{V} \, [\, x_1^2(1-C_{11}) + 2x_1x_2(1-C_{12})$$

$$+ \, x_2^2(1-C_{22})\,] \qquad (2\text{-}59)$$

$$\frac{\partial}{\partial V} \, (\frac{\partial A}{\partial N_1} \, \Big|_{T,V,N_2})\, \Big|_{T,\underline{N}} \;=\; - \frac{\partial P}{\partial N_1} \, \Big|_{T,V,N_2}$$

$$= \frac{RT}{V} \, [\, x_1(1-C_{11}) + x_2(1-C_{12})\,]$$

$$(2\text{-}60)$$

$$\frac{\partial^2 A}{\partial N_1^2} \, \Big|_{T,V,N_2} \;=\; \frac{\partial \mu_1}{\partial N_1} \, \Big|_{T,V,N_2}$$

$$= \frac{RT}{V} \, [\, \frac{1}{\rho_1} - \frac{C_{11}}{\rho}\,] \qquad (2\text{-}61)$$

For symmetric matrices, the first positive definite condition to break is the determinant condition. Hence, the spinodal for a binary system is defined as that locus of points satisfying

$$\begin{vmatrix} \dfrac{\partial^2 A}{\partial V^2} & \dfrac{\partial^2 A}{\partial N_1 \partial V} \\[3ex] \dfrac{\partial^2 A}{\partial V \partial N_1} & \dfrac{\partial^2 A}{\partial N_1^2} \end{vmatrix} \;=\; 0 \qquad (2\text{-}62)$$

Using equations (2-59), (2-60), and (2-61) in equation (2-62), we get the following relation between the direct correlation function integrals at the spinodal curve

$$x_1 C_{11} + x_2 C_{22} - x_1 x_2 (C_{11} C_{22} - C_{12}^2) = 1 \qquad (2\text{-}63)$$

For a binary system, the stability criterion when working with pressure, temperature, and mole fraction as independent variables is (Prausnitz, 1969)

$$\left. \frac{\partial^2 g}{\partial x_1^2} \right|_{TP} > 0 \qquad (2\text{-}64)$$

where g is the molar free energy of Gibbs. Equation (2-64) also leads to equation (2-63). A similar expression is obtained for multicomponent systems,

$$\begin{vmatrix} \dfrac{\partial^2 g}{\partial x_1^2} & \cdots & \dfrac{\partial^2 g}{\partial x_{n-1} \partial x_1} \\ \vdots & & \\ \dfrac{\partial^2 g}{\partial x_{n-1} \partial x_1} & \cdots & \dfrac{\partial^2 g}{\partial x_{n-1}^2} \end{vmatrix} > 0 \qquad (2\text{-}65)$$

with all its principal minors greater than zero.

It might be simpler to check stability with the Gibbs free energy, but then $(n-1)^2/2 + (n-1)/2$ second derivatives must be evaluated to check the main determinant. With the Helmholtz free energy, for a given pressure, temperature

and composition, the framework of the fluctuation theory can be used directly. The only difficulty is that the density of the solution must be found using equation (2-29).

For the two pure component points in the mixture, equation (2-63) reduces to

$$C_{ii} = 1 \qquad\qquad (2-66)$$

and with the aid of equation (2-59) we can say that in a pure component the spinodal is defined as that locus of points satisfying the limit of mechanical stability.

In practice, equation (2-62) may be of little utility because equations for multicomponent mixtures have many more terms to handle.

CHAPTER 3
DIRECT CORRELATION FUNCTION INTEGRALS FROM
EXPERIMENTS AND CORRELATION

3.1 Introduction

A major motivation for studying the fluctuation solu-
tion theory approach is that direct correlation function
integrals may be relatively simple and universal functions
of number density (or density at macroscopic level). A
general microscopic approach to prove this point is not
our intention. Rather, we examine macroscopic experimental
information about the integrals. It is worth noting that
the relation of the integrals to experimental information
is through derivatives of thermodynamic properties. As
will be seen in Section 3.2 the integrals are related to
the isothermal compressibility, partial molar volumes of
components in a mixture, and second derivative of the
excess Gibbs free energy. This kind of dependence can
make evaluation somewhat difficult.

Section 3.2 presents equations and results for ideal
mixtures. Section 3.3 does the same with nonideal mixtures.
Finally, Section 3.4 shows how changing parameter values
in excess Gibbs free energy models affect the form of
the direct correlation function integrals.

3.2 Experimental Behavior of Ideal Mixtures

Thermodynamic properties of binary systems are completely defined by C_{11}, C_{12}, and C_{22}. Equations (2-32) and (2-26) are the starting point through the expressions

$$\left. \frac{\partial \ln \gamma_i}{\partial \rho_j} \right|_{T,\rho_{k \neq j}} = \frac{(1 - C_{ij})}{\rho} \qquad i,j = 1,2 \qquad (3-1)$$

$$\left. \frac{\partial \ P/RT}{\partial \rho_j} \right|_{T,\rho_{k \neq j}} = 1 - \sum_{i=1}^{2} x_i C_{ij} \qquad (3-2)$$

We want to find an expression for the composition variation of the direct correlation function integral. Operating on equations (3-1) and (3-2) we get

$$\frac{v}{\kappa RT} = 1 - x_1^2 C_{11} - x_2^2 C_{22} - 2x_1 x_2 C_{12} \qquad (3-3)$$

$$\frac{\overline{v}_1}{\kappa RT} = 1 - x_1 C_{11} - x_2 C_{12} \qquad (3-4)$$

$$\left. \frac{\partial \ln \gamma_1}{\partial x_1} \right|_{T,P} = x_2 [(1-C_{11})(1-C_{22}) - (1-C_{12})^2] \frac{\kappa RT}{v} \qquad (3-5)$$

We can rearrange these last equations to obtain

$$(1 - C_{11}) = \frac{\overline{v}_1^2}{v \kappa RT} + x_2 \left. \frac{d \ln \gamma_1}{dx_1} \right|_{T,P} \qquad (3-6)$$

$$(1 - C_{12}) = \frac{\overline{V}_1 \overline{V}_2}{v \kappa RT} - x_1 \left. \frac{d \ln \gamma_1}{dx_1} \right|_{T,P} \qquad (3-7)$$

$$(1 - C_{22}) = \frac{\overline{V}_2^2}{v \kappa RT} + x_1 \left. \frac{d \ln \gamma_2}{dx_2} \right|_{T,P} \qquad (3-8)$$

The experimental behavior of the direct correlation integrals can be determined through simultaneous knowledge of isothermal compressibility, molar volume, partial molar volume, and partial derivative of the logarithm of the activity coefficient. This is the pure component molar volume as a function of pressure and the excess Gibbs free energy as a function of composition and pressure. The excess Gibbs free energy is related to the activity coefficient by

$$g^E = \frac{G^E}{RT}$$

$$= x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \qquad (3-9)$$

where the g^E values are generally found from a model whose parameters are obtained from phase equilibrium and density data. Taking the derivative with respect to mole fraction of component 1 twice, we get

$$\left. \frac{\partial^2 g^E}{\partial x_1^2} \right|_{T,P} = \frac{1}{x_2} \left. \frac{\partial \ln \gamma_1}{\partial x_1} \right|_{T,P} \qquad (3-10)$$

$$= \frac{1}{x_1} \left. \frac{\partial \ln \gamma_2}{\partial x_2} \right|_{T,P} \qquad (3-11)$$

The partial molar volumes are obtained from the excess volume by

$$\bar{V}_1 = v_1^o + x_2 \left.\frac{\partial v^E}{\partial x_1}\right|_{T,P} \qquad (3\text{-}12)$$

$$\bar{V}_2 = v_2^o + x_1 \left.\frac{\partial v^E}{\partial x_2}\right|_{T,P} \qquad (3\text{-}13)$$

The isothermal compressibility is related to the excess molar volume by

$$-\frac{1}{v} \left.\frac{\partial v^E}{\partial P}\right|_{T,x_1} = \kappa^E \qquad (3\text{-}14)$$

where κ^E is related to the solution isothermal compressibility by

$$\kappa = \phi_{V_1} \kappa_1^o + \phi_{V_2} \kappa_2^o + \kappa^E \qquad (3\text{-}15)$$

with ϕ_{V_1} as the molar volume fraction.

For an ideal solution equations (3.6) to (3.8) become

$$(1 - C_{11}^{id}) = \frac{v_1^{o^2}}{v\kappa RT} \qquad (3\text{-}16)$$

$$(1 - C_{12}^{id}) = \frac{v_1^{o^2} v_2^{o^2}}{v\kappa RT} \qquad (3\text{-}17)$$

$$(1 - C_{22}^{id}) = \frac{v_2^{o^2}}{v\kappa RT} \qquad (3\text{-}18)$$

From these equations it is apparent that the direct correlation function integrals (c_{11}^{id}, c_{12}^{id}, c_{22}^{id}) are not independent; they are related by

$$(1 - c_{12}^{id})^2 = (1 - c_{11}^{id})(1 - c_{22}^{id}) \qquad (3-19)$$

If the result of equation (3-19) is used in equation (3-5), the definition of ideal solution is recovered. We can write the product of isothermal compressibility times molar volume as

$$v\kappa = -\left(x_1 \left. \frac{\partial v_1^O}{\partial P} \right|_{T,x_1} + x_2 \left. \frac{\partial v_2^O}{\partial P} \right|_{T,x_1} + \left. \frac{\partial v^E}{\partial P} \right|_{T,x_1} \right)$$

$$= x_1 v_1^O \kappa_1^O + x_2 v_2^O \kappa_2^O + \frac{\partial v^E}{\partial P} \qquad (3-20)$$

In the case of an ideal mixture the last term in equation (3-20) is zero. Using equation (3-20), we can rewrite equation (3-16) to (3-18) as

$$\frac{1}{(1 - c_{11}^{id})} = RT \left(x_1 \frac{\kappa_1^O}{v_1^O} + x_2 \frac{\kappa_2^O \, v_2^O}{v_1^O} \right) \qquad (3-21)$$

$$\frac{1}{(1 - c_{12}^{id})} = RT \left(x_1 \frac{\kappa_1^O}{v_2^O} + x_2 \frac{\kappa_2^O}{v_1^O} \right) \qquad (3-22)$$

$$\frac{1}{(1 - c_{22}^{id})} = RT \left(x_1 \frac{\kappa_1^O \, v_1^O}{v_2^{O^2}} + \frac{\kappa_2^O}{v_2^O} \right) \qquad (3-23)$$

These equations show that at constant pressure and constant temperature the inverse of the direct correlation function integrals is a linear function in mole fraction.

Table 3-1 presents the direct correlation function integrals for n-heptane--n-octane, chosen as representative of ideal mixture, at different temperatures. A good indication of solution ideality is the agreement between C_{22} experimental and C_{22} calculated using equation (3-19). Since this indicates correlation within experimental error, the n-heptane--n-octane system is ideal. Figure 3-1 shows the shape of the direct correlation function integrals which are not linear in mole fraction. Figure 3-2 confirms the ideality of the system showing a linear variation of the inverse of $(1-C_{ij})$ with mole fraction. Table 3-2 shows that the same low pressure behavior is observed at high pressure. Tables 3-3 to 3-10 present direct correlation function integrals for different ideal systems. In all these data, differences between C_{22} experimental and C_{22} calculated are probably within experimental error (which is 0.5-3.% in κ). Thus we can conclude that these systems are essentially ideal. Another possible indicator of ideality would be the correlation coefficient for linear fitting, r, of $\frac{1}{(1-C_{11})}$ as a function of x_1. In the above systems, r is very close to unity, containing ideal behavior. However, as shown below, such correlations also arise in nonideal systems, meaning that linear correlation is not useful in discriminating nonideality.

Table 3-1

Test for ideality of n-Heptane (1)--n-Octane (2) at Various Temperatures, P = 1 atm

T, K	x_1	κ, atm^{-1} × 10^{+4}	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
273.15	0.0	1.012	158.65	55.63	61.94	68.95	68.95
	0.1727	1.045	155.90	54.80	61.03	67.93	67.95
	0.3463	1.077	153.14	54.12	60.27	67.09	67.11
	0.5870	1.120	149.32	53.37	59.42	66.15	66.17
	0.7796	1.155	146.25	52.82	58.82	65.48	65.49
	1.0000	1.196	142.75	52.26	58.19	64.77	64.78
	$r(C_{11})$ = .995						
298.15	0.0	1.215	163.72	43.52	48.52	54.08	54.09
	0.1727	1.253	160.87	42.93	47.87	53.36	53.37
	0.3463	1.289	158.00	42.48	47.37	52.80	52.82
	0.5870	1.346	154.02	41.72	46.52	51.85	51.87
	0.7796	1.391	150.83	41.21	45.95	51.22	51.23
	1.0000	1.444	147.19	40.67	45.35	50.55	50.57
	$r(C_{11})$ = .999						
313.15	0.0	1.354	166.95	37.74	42.12	46.99	47.00
	0.1727	1.398	164.03	37.19	41.51	46.30	46.33
	0.3463	1.443	161.09	36.68	40.94	45.67	45.69
	0.5870	1.509	157.01	35.97	40.14	44.78	44.79
	0.7796	1.559	153.75	35.54	39.67	44.25	44.27
	1.0000	1.618	150.02	35.08	39.16	43.68	43.71
	$r(C_{11})$ = .998						

$r(C_{11})$ is the correlation coefficient for the inverse of $(1-C_{11})$.
$-C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are from Eduljee et al. (1951).
Activity coefficient values are obtained from Solubility Parameter Theory.
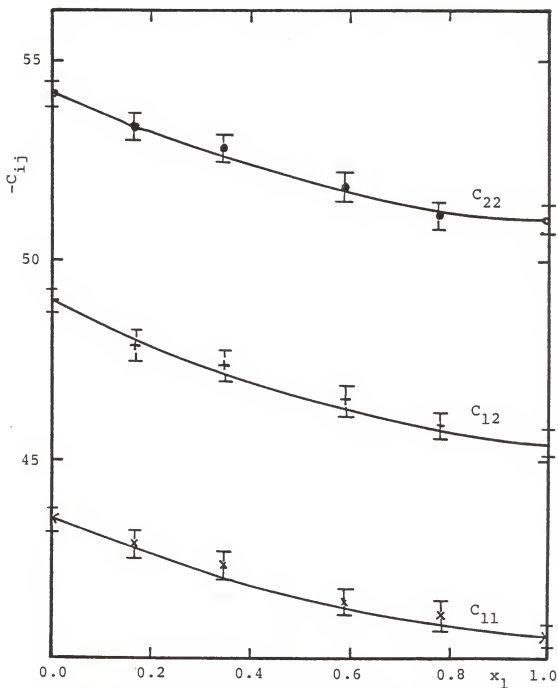
Figure 3-1. Direct correlation function integrals
(DCFI) in n-heptane (1)--n-octane (2)
at 298.15 K and 1 atm ($\bullet$, x, + data
from references in Table 3-1, ———
smoothed).

Table 3-2

Test for Ideality of n-Heptane (1)--n-Octane (2) at Various Pressures, T = 298.15 K

P, atm	x_1	κ, atm^{-1} x10^{+4}	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
2500	0.00	0.333	141.49	135.12	152.89	172.65	172.97
	0.25	0.337	137.46	137.43	155.46	175.50	175.84
	0.50	0.342	133.43	139.81	158.11	178.46	178.78
	0.75	0.346	129.39	142.28	160.87	181.54	181.87
	1.00	0.351	125.33	144.85	163.73	184.74	185.05
	$r(C_{11})$ = -.999						
5000	0.00	0.201	132.73	208.68	237.06	268.43	269.28
	0.25	0.203	128.87	213.21	242.05	273.94	274.77
	0.50	0.205	124.99	217.89	247.21	279.65	280.46
	0.75	0.207	121.12	222.74	252.57	285.59	286.37
	1.00	0.209	117.23	227.77	258.15	291.79	292.56
	$r(C_{11})$ = -.999						

$r(C_{11})$ is the correlation coefficient for the inverse of $(1-C_{11})$.
$-C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility and activity coefficient data are from same sources as Table 3-1.
High pressure data are from Eduljee et al. (1951).
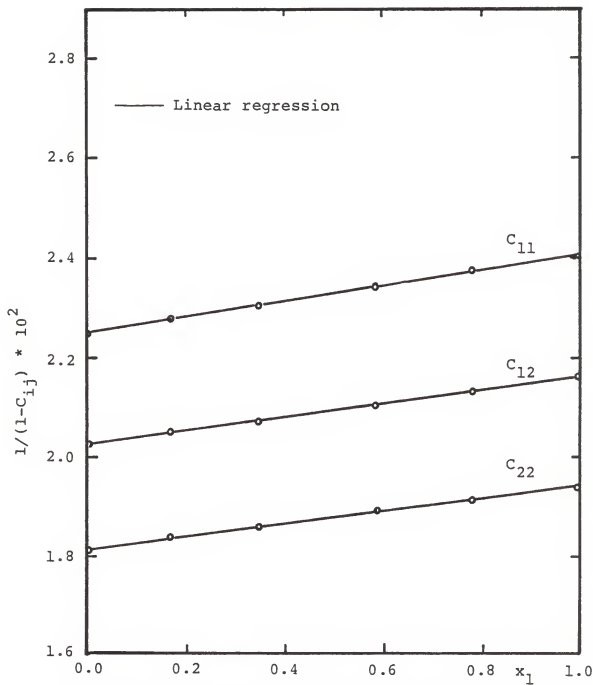
Figure 3-2. Inverse DCFI in n-heptane (1)--n-octane (2) at 298.15 K and 1 atm. Data as Figure 3-1.

Table 3-3

Test for Ideality of n-Hexane (1)--n-Heptane (2) at Various Temperatures, P = 1 atm

T, K	x_1	κ, atm^{-1} x 10^{+4}	v, cc/mol	$-C_{12}$	$-C_{11}$	$-C_{22}$	$-C_{22,calc}$
273.15	0.0	1.196	142.75	46.39	41.16	52.26	52.26
	0.3427	1.237	137.36	46.62	41.36	52.51	52.53
	0.6807	1.280	132.04	46.87	41.59	52.79	52.80
	1.0000	1.321	127.02	47.22	41.90	53.17	53.19
	$r(C_{11}) = -.993$						
298.15	0.0	1.444	147.19	36.16	32.13	40.67	40.68
	0.3427	1.505	141.73	36.03	32.01	40.52	40.54
	0.6807	1.567	136.35	35.97	31.96	40.44	40.46
	1.0000	1.629	131.26	35.93	31.93	40.40	40.41
	$r(C_{11}) = .957$						
313.15	0.0	1.618	150.02	31.25	27.82	35.09	35.09
	0.3427	1.696	144.56	30.93	27.53	34.72	34.73
	0.6807	1.775	139.18	30.69	27.33	34.45	34.45
	1.0000	1.855	134.09	30.48	27.13	34.20	34.22
	$r(C_{11}) = .997$						
333.15	0.0	1.891	154.03	25.73	22.98	28.80	28.79
	0.3427	1.999	148.61	25.22	22.52	28.22	28.23
	0.6807	2.111	143.26	24.75	22.11	27.69	27.69
	1.0000	2.222	138.21	24.36	21.75	27.25	27.26
	$r(C_{11}) = .999$						

$r(C_{11})$ is the correlation coefficient for the inverse of $(1-C_{11})$.
$-C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are from Eduljee et al. (1951).
Activity coefficient values are obtained from Solubility Parameter Theory.

Table 3-4

Test for Ideality of n-Hexane (1)--n-Octane (2) at Various Temperatures, P = 1 atm

T, K	x_1	κ, atm^{-1} x 10^{+4}	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
273.15	.00	1.012	158.65	43.81	55.00	68.95	68.98
	.3852	1.125	146.47	42.68	53.57	67.15	67.17
	.6618	1.211	137.72	42.16	52.92	66.32	66.36
	1.0000	1.311	127.02	41.90	52.58	65.88	65.92
	$r(C_{11})$ = .967						
298.15	.0	1.215	163.72	34.38	43.16	54.08	54.11
	.3852	1.362	151.22	33.19	41.66	54.20	52.22
	.6618	1.478	142.24	32.50	40.79	51.11	51.13
	1.0000	1.629	131.26	31.94	40.08	50.20	50.23
	$r(C_{11})$ = .992						
313.15	.0	1.354	166.95	29.94	37.54	46.99	47.00
	.3852	1.579	154.29	27.71	34.77	43.52	43.57
	.6618	1.603	145.20	29.06	36.44	45.60	45.63
	1.0000	1.855	134.09	27.13	34.03	42.57	42.62
	$r(C_{11})$ = .751						

$r(C_{11})$ is the correlation coefficient for the inverse of $(1-C_{11})$.
$-C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are from Eduljee et al. (1951).
Activity coefficient values are obtained from Solubility Parameter Theory.

Table 3-5

Test for Ideality of Tetraethylmethane (1)-Tetrapropylmethane (2) at Various
Temperatures, p = 1 atm

T, K	x_1	κ, atm^{-1} x 10^4	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
303.15	0.0	0.995	240.20	48.16	68.08	96.05	96.07
	0.5	1.010	205.73	55.88	78.62	110.44	110.45
	1.0	1.083	171.87	62.80	87.51	121.77	121.79
313.5	0.0	1.062	242.41	44.06	62.28	87.84	87.87
	0.5	1.114	207.68	49.44	69.55	97.69	97.68
	1.0	1.177	173.57	56.39	78.57	109.31	109.32
323.15	0.0	1.149	244.68	39.80	56.23	79.29	79.28
	0.5	1.201	209.69	44.80	63.02	88.48	88.49
	1.0	1.257	175.32	51.59	71.87	99.96	99.97
333.15	0.0	1.234	247.00	36.28	51.25	72.23	72.23
	0.5	1.288	212.06	40.89	57.50	80.70	80.70
	1.0	1.365	177.12	46.47	64.74	90.04	90.04
343.15	0.0	1.323	249.39	33.15	46.82	65.95	65.96
	0.5	1.403	214.18	36.74	51.67	72.50	72.51
	1.0	1.475	178.97	42.09	58.65	81.56	81.57
353.15	0.0	1.432	251.85	30.00	42.38	59.69	59.70
	0.5	1.492	216.00	33.87	47.62	66.79	66.79
	1.0	1.578	180.89	38.56	53.71	74.65	74.66
363.15	0.0	1.523	254.36	27.70	39.11	55.05	55.06
	0.5	1.610	218.33	30.80	43.29	60.68	60.68
	1.0	1.711	182.87	34.87	48.58	67.51	67.53

$-C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are from Grindley (1973).
Activity coefficient values are obtained from Solubility Parameter Theory.

Table 3-6

Test for Ideality of Benzene (1)-Cyclohexane (2) at Various Temperatures, P = 1 atm

T, K	x_1	κ, atm^{-1} × 10^{+4}	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
298.15	.0	1.155	108.76	26.30	31.58	37.49	37.78
	.2886	1.146	103.71	27.14	33.06	39.83	40.22
	.5489	1.097	98.77	29.41	36.24	44.20	44.63
	.7850	1.046	93.98	32.29	40.13	49.41	49.82
	1.0000	0.978	89.39	36.36	45.47	56.31	56.80
	$r(C_{11})$ = −.977						
310.65	.0	1.284	110.46	22.92	27.57	32.75	33.12
	.2889	1.262	104.77	23.88	29.15	35.15	35.54
	.5493	1.216	99.65	25.73	31.75	38.75	39.12
	.7853	1.155	95.01	28.38	35.30	43.56	43.84
	1.0000	1.105	90.78	31.23	39.04	48.26	48.74
	$r(C_{11})$ = −.985						
323.15	.0	1.434	112.24	19.88	23.98	28.52	28.88
	.2889	1.404	106.99	20.00	25.46	30.74	31.12
	.5494	1.355	101.86	22.40	27.71	33.84	34.22
	.7853	1.284	96.91	24.81	30.88	38.01	38.38
	1.0000	1.207	92.23	27.82	34.73	42.83	43.30
	$r(C_{11})$ = −.983						
335.64	.0	1.808	116.14	17.29	20.93	24.95	25.29
	.2886	1.743	110.14	17.98	22.10	26.74	27.11
	.5489	1.702	104.71	19.42	24.09	29.46	29.83
	.7850	1.608	99.80	21.69	27.02	33.24	33.60
	1.0000	1.519	95.33	24.92	31.04	38.17	38.60
	$r(C_{11})$ = −.974						

$r(C_{11})$ is the correlation coefficient for the inverse of $(1-C_{11})$.

$-C_{22,calc}$ is the value obtained using equation (3-19).

Isothermal compressibility data are from Holder and Whalley (1962).

Activity coefficient values are obtained from Solubility Parameter Theory.

Volumetric data are from Wood and Austin (1945).

Table 3-7

Test for Ideality of Carbontetrachloride (1)-Benzene (2) at Various Temperatures, P = 1 atm

T, K	x_1	κ, atm^{-1} x 10^4	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
313.15	0.	1.120	91.07	36.29	33.45	30.65	30.83
	0.2	1.149	92.63	34.69	31.98	29.32	29.47
	0.4	1.174	94.19	33.35	30.73	28.19	28.31
	0.6	1.204	95.75	31.97	29.44	26.99	27.14
	0.8	1.225	97.32	30.91	28.43	26.04	26.14
	1.0	1.235	98.88	30.16	27.69	25.37	25.41
	$r(C_{11}) = .997$						
323.15	0.	1.206	92.23	33.03	30.43	27.84	28.03
	0.2	1.242	93.86	31.45	28.97	26.52	26.68
	0.4	1.273	95.46	30.11	27.74	25.41	25.55
	0.6	1.310	97.03	28.74	26.47	24.26	24.37
	0.8	1.331	98.59	27.82	25.61	23.45	23.57
	1.0	1.337	100.15	27.25	25.05	22.95	23.02
	$r(C_{11}) = .977$						
343.15	0.	1.392	94.68	27.61	25.37	23.16	23.30
	0.2	1.461	96.41	25.79	23.68	21.65	21.74
	0.4	1.518	98.10	24.31	22.33	20.40	20.50
	0.6	1.557	99.74	23.23	21.37	19.56	19.65
	0.8	1.577	101.33	22.52	20.76	19.06	19.13
	1.0	1.563	102.84	22.37	20.68	19.07	19.11
	$r(C_{11}) = .973$						

$r(C_{11})$ is the correlation coefficient for the inverse of $(1-C_{11})$.
$-C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are from Holder and Whalley (1962).
Activity coefficient values are obtained from Van Laar equation.
Parameters are from
Volumetric data are from Wood and Brusie (1943).

Table 3-8

Test for Ideality of Benzene (1)-Isooctane (2) at Various Temperatures, P = 1 atm

T, K	x_1	κ, atm^{-1} x10^4	V, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
298.15	0.0	1.488	165.88	12.52	24.11	44.56	45.63
	0.2	1.428	150.91	14.32	27.64	51.23	52.54
	0.4	1.353	135.78	16.84	32.49	60.33	61.87
	0.6	1.260	120.49	20.51	39.52	73.32	75.33
	0.8	1.140	105.04	26.28	50.41	93.17	95.88
	1.0	0.978	89.40	36.37	69.34	126.94	131.40
	$r(C_{11})$ = -.999						
310.65	0.0	1.654	168.42	10.85	21.03	38.95	39.95
	0.2	1.589	153.22	12.41	24.09	44.74	45.94
	0.4	1.509	137.87	14.58	28.30	52.60	54.10
	0.6	1.408	122.35	17.75	34.35	63.77	65.65
	0.8	1.279	106.67	22.68	43.68	80.67	83.30
	1.0	1.105	90.79	31.23	59.65	108.89	113.13
	$r(C_{11})$ = -.999						
323.15	0.0	1.849	171.08	9.34	18.25	33.90	34.84
	0.2	1.773	155.31	10.72	20.97	39.03	40.18
	0.4	1.679	139.54	12.66	24.72	46.02	47.43
	0.6	1.562	123.77	15.50	30.16	56.01	57.84
	0.8	1.410	108.01	19.97	38.59	71.24	73.74
	1.0	1.207	92.24	27.82	53.21	96.97	100.97
	$r(C_{11})$ = -.999						

$r(C_{11})$ is the correlation coefficient for the inverse of $(1-C_{11})$.
$-C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are calculated from Brelvi and O'Connell (1975).
Activity coefficient values are obtained from Wilson equation.
Parameters are from Prausnitz et al. (1967).
Volumetric data are from Wood and Sandus (1956).

Table 3-9

Test for Ideality of Cyclohexane (1)-Cycloheptane (2), P = 1 atm

T, K	x_1	κ, $TP_a^{-1} \times 10^9$	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
298.15	0.0	0.9220	121.73	41.46	46.56	52.26	52.27
	0.1	0.9422	120.43	41.01	46.04	51.68	51.67
	0.2	0.9620	119.12	40.59	45.58	51.16	51.16
	0.3	0.9816	117.82	40.22	45.16	50.67	50.69
	0.4	1.001	116.52	39.88	44.77	50.22	50.24
	0.5	1.021	115.22	39.55	44.40	49.79	49.83
	0.6	1.041	113.92	39.23	44.03	49.37	49.40
	0.7	1.061	112.63	38.91	43.67	48.94	48.99
	0.8	1.083	111.33	38.57	43.28	48.50	48.55
	0.9	1.106	110.05	38.22	42.87	48.02	48.07
	1.0	1.130	108.77	37.83	42.43	47.50	47.53

$r(C_{11})$ = .999

$r(C_{11})$ is the correlation coefficient for the inverse of $(1-C_{11})$.
$-C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility, activity coefficient and volumetric data are from
Ewing and Marsh (1974a).

Table 3-10

Test for Ideality of Cyclohexane (1)-2-3 Dimethylbutane (2), P = 1 atm

T, K	x_1	κ, TPa^{-1} x10^9	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
298.15	0.0	1.797	131.22	19.35	23.31	28.46	28.04
	0.1	1.718	128.93	20.52	24.87	30.35	30.10
	0.2	1.645	126.65	21.80	26.54	32.35	32.26
	0.3	1.575	124.39	23.21	28.33	34.45	34.53
	0.4	1.507	122.13	24.76	30.24	36.68	36.88
	0.5	1.442	119.88	26.45	32.30	39.06	39.40
	0.6	1.378	117.63	28.31	34.34	41.62	42.09
	0.7	1.315	115.40	30.36	36.97	44.40	44.97
	0.8	1.252	113.18	32.63	39.63	47.42	48.08
	0.9	1.190	110.96	35.12	42.53	50.70	51.46
	1.0	1.130	108.76	37.83	45.65	54.20	55.04

$$r(C_{11}) = -.999$$

$r(C_{11})$ is the correlation coefficient for the inverse of $(1-C_{11})$.
$-C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility, activity coefficient and volumetric data are from Ewing and Marsh (1974b).

3.3 Experimental Behavior of Nonideal Mixtures

We have chosen the acetone-carbon disulphide system as representative of a nonideal mixture.

Winnick and Powers (1966a,b) made a detailed study of this mixture at low and high pressure. There is information to calculate excess Gibbs free energy, excess molar volume, and excess isothermal compressibility. With these data and equations (3-6) to (3-8) we can obtain the direct correlation function integrals for this system. Table 3-11 presents results at atmospheric pressure and a temperature of 273.15 K using Winnick and Powers' equations. For the free energy at atmospheric pressure, they used the vapor pressure data of Zawidsky (1900) and a fourth order equation to smooth the free energy values. In order to convert the data from 298.23 K to 273.15 K, they used the calormetric data of Schmidt (1926) and Staveley et al. (1955). The correlation coefficient of the linear fitting of the inverse of $(1-C_{11})$ is almost one indicating behavior near ideal. But the difference between the experimental and the calculated direct correlation function integrals for a pair of carbon disulphide molecules is large (from 20 to 100%). Figure 3-3 shows the particular shape of C_{11}, C_{12}, and C_{22}. Figure 3-4 presents the inverse of $(1-C_{ij})$ which shows that the linear fitting is not really good. The points do not form straight lines at all. The extreme points of the linear fitting at mole fraction zero or one are not

Table 3-11

Test for Nonideality of Acetone (1)-Carbon Disulphide (2), P = 1 atm
Using Equations of Winnick and Powers

T, K	x_1	κ, atm^{-1} x 10^4	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
273.15	0.	0.782	58.87	40.06	42.12	32.56	44.28
	0.1	0.827	60.48	41.71	38.87	29.87	36.22
	0.2	0.870	61.99	40.69	35.80	27.62	31.50
	0.3	0.911	63.42	38.58	33.24	25.71	28.64
	0.4	0.949	64.80	36.32	31.21	24.02	26.82
	0.5	0.982	66.13	34.35	29.59	22.53	25.49
	0.6	1.009	67.40	32.80	28.25	21.36	24.33
	0.7	1.027	68.60	31.60	27.21	20.73	23.43
	0.8	1.035	69.70	30.73	26.66	20.59	23.13
	0.9	1.032	70.66	30.25	26.84	19.74	23.81
	1.0	1.018	71.43	30.30	27.44	13.29	24.85

$r(C_{11}) = .973$

$r(C_{11})$ is the correlation coefficient for the inverse of $(1-C_{11})$.
$C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are from Winnick and Powers (1966a).
Activity coefficient values are from Winnick and Powers (1966b).
Volumetric data are from Winnick and Powers (1966a).
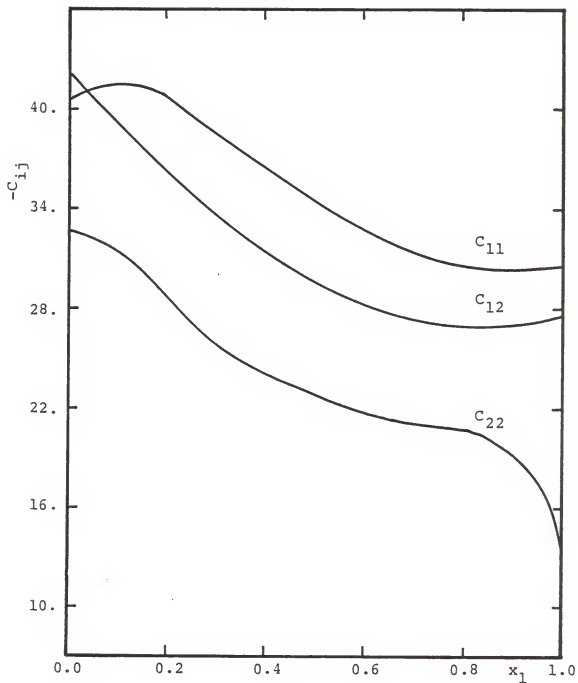
Figure 3-3. DCFI in acetone (1)-carbon disulphide (2) at 273.15 K and 1 atm using equations of Winnick and Powers (1966a,b).
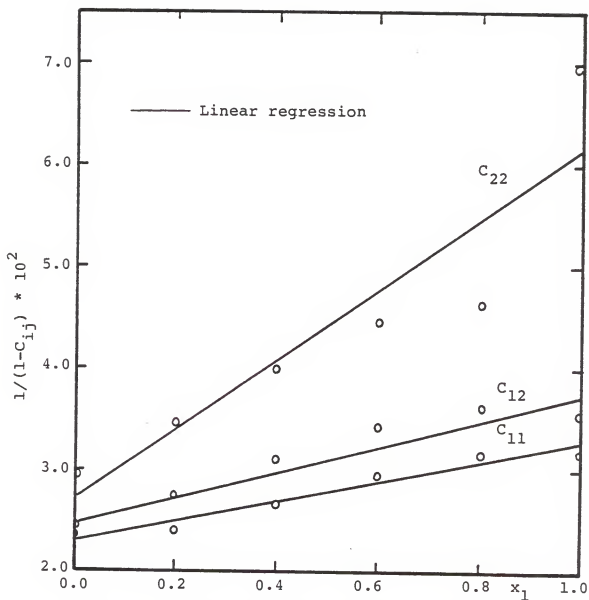
Figure 3-4. Inverse DCFI in acetone (1)-carbon disulphide (2) at 273.15 K and 1 atm using equations of Winnick and Powers (1966a,b).

coincident with the values of pure component calculations.
For example, at acetone mole fraction equal to zero, the
experimental value is 2.98E-2 and the linear regression
value is 2.71E-2. The conclusion, already mentioned, is
that the correlation coefficient alone is not a good indi-
cator of nonideality. On the other hand, the differences
between the experimental and calculated C_{22} indicate that
the mixture is not ideal.

It is apparent from the curve in Figure 3-3 that direct
correlation function integrals are not likely to be modelled.
It is possible that a problem could be in the experimental
isothermal compressibility. Figure 3-5 shows the smoothed
curve of Winnick and Powers (1966a) for the isothermal com-
pressibility as function of mole fraction used to evaluate
C_{ij}. There is a discrepancy at the pure acetone side that
could change the form of the curve. An alternative fitting
of the data would change the results near the pure acetone
side. However, any such change would be very small near the
pure carbon disulphide side where C_{11} goes through an un-
expected maximum.

The above values were obtained using the polynomial
fit of Winnick and Powers (1966b) to experimental Gibbs
free energy. Another way to do this is with a model.
Since the acetone-carbon disulphide system is close to but
not at immiscibility, the Wilson equation is appropriate
to describe the nonideality, and the results of this method
will be adopted as representative of this system. Table
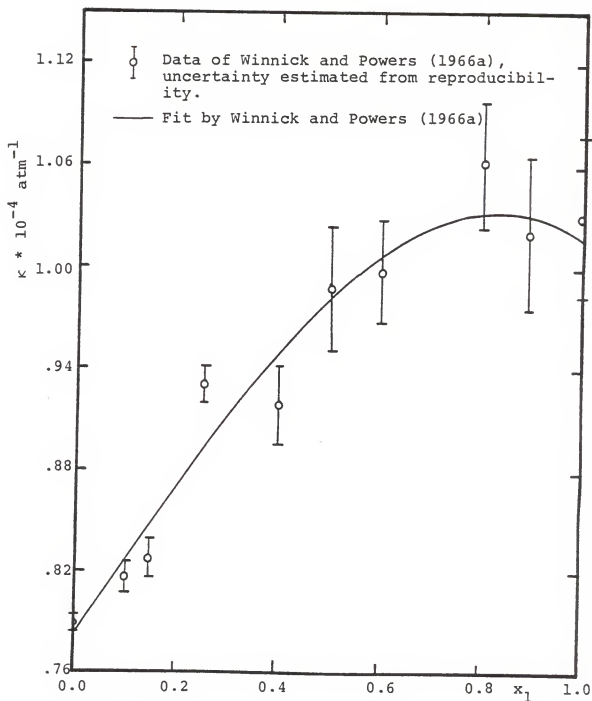
Figure 3-5. Experimental isothermal compressibilities of acetone (1)-carbon disulphide (2) at 273.15 K and 1 atm.

3-12 presents values of derivatives of activity coeffi-
cients using Winnick and Powers' polynomial and the Wilson
equation. Table 3-13 and Figure 3-6 present results for
the same calculation. There is no maximum in C_{11}, and
the shape resembles that of ideal mixtures. Figure 3-7
presents the inverses of the $(1-C_{ij})$. The high values of
the derivatives at infinite dilution explain the differ-
ence in C_{ij} obtained using equations (3-6) to (3-8) with
Winnick and Powers' data. Before discussing the conse-
quences of this for further modelling, we show the results
of many more nonideal systems in Tables 3-14 to 3-29.

These results show two important features. First,
there are some systems with extrema in the C_{ij}. Second,
there are some systems where the C_{ij} values cross as a
function of composition.

3.4 Nonideal Behavior from Excess Gibbs Energy Models

As shown above, the results for the C_{ij} are sensitive
to the model used to describe nonideal behavior of mixtures.
This section gives some analytic results for common g^E
models.

The simplest model for g^E is a two-suffix Margules
equation; mixtures that follow this equation are known as
quadratic mixtures. The starting equation for binary
mixtures is

Table 3-12

Derivatives of Activity Coefficients for Acetone (1)-Carbon Disulphide (2), P = 1 atm

(a) Using Equation of Winnick and Powers

T, K	x_1	v, cc/mol	$\bar{V}_1$, cc/mol	$\bar{V}_2$, cc/mol	d ln γ_1/dx_1	d ln γ_2/dx_2
273.15	0.00	58.67	75.56	58.67	-14.324	0.000
	0.25	62.56	73.48	58.92	- 3.158	-1.053
	0.50	66.03	72.65	59.41	- 1.733	-1.733
	0.75	69.12	71.92	60.72	- 0.680	-2.040
	1.00	71.43	71.43	64.67	0.000	-11.544

(b) Using Wilson equation

T, K	x_1	v, cc/mol	$\bar{V}_1$, cc/mol	$\bar{V}_2$, cc/mol	d ln γ_1/dx_1	d ln γ_2/dx_2
273.15	0.00	58.67	75.56	58.67	-7.952	0.000
	0.25	62.56	73.48	58.92	-2.936	-0.979
	0.50	66.03	72.65	59.41	-1.541	-1.541
	0.75	69.12	71.92	60.72	-0.777	-2.331
	1.00	71.43	71.43	64.67	0.000	-3.924

Table 3-13

Test for Nonideality of Acetone (1)-Carbon Disulphide (2) at Various Temperatures, P = 1 atm. Using Wilson Equation for Excess Gibbs Energy

T, K	x_1	κ, atm^{-1} x 10^4	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
273.15	0.00	0.782	58.87	46.58	42.11	32.47	38.07
	0.25	0.891	62.71	40.02	34.39	26.54	29.55
	0.50	0.982	66.13	34.54	29.47	22.52	25.14
	0.75	1.033	69.17	31.13	26.87	20.29	23.19
	1.00	1.018	71.43	30.31	27.34	20.73	24.66
	$r(C_{11})$ = .981						
293.15	0.00	0.925	60.28	33.84	32.72	26.09	31.64
	0.20	1.024	63.48	33.97	29.16	22.00	25.78
	0.40	1.107	66.64	29.96	25.60	19.30	21.85
	0.80	1.160	71.36	25.84	22.94	17.48	20.35
	1.00	1.245	73.29	23.47	19.98	13.42	16.99
	$r(C_{11})$ = .981						
303.15	0.00	0.994	60.99	30.25	29.64	23.67	30.03
	0.20	1.090	63.67	31.23	26.83	20.10	23.03
	0.40	1.188	66.34	27.29	23.34	17.44	19.94
	0.80	1.324	71.69	22.04	19.59	14.61	17.40
	1.00	1.362	74.37	20.95	17.55	11.28	14.68
	$r(C_{11})$ = .971						
313.15	0.00	1.070	61.76	31.49	28.60	21.47	25.97
	0.20	1.188	64.51	27.18	23.97	18.17	21.12
	0.40	1.297	67.25	24.01	20.89	15.66	18.16
	0.80	1.440	72.73	20.03	17.47	12.53	15.22
	1.00	1.483	75.48	18.81	17.18	12.46	15.68
	$r(C_{11})$ = .997						

$r(C_{11})$ is the correlation coefficient for the inverse of $(1-C_{11})$.
C_{11} calc is the value obtained using equation (3-19).
Isothermal compressibility data are from Winnick and Power (1966a).
Activity coefficient values are obtained from Wilson equation.
Parameters are from Prausnitz et al. (1967).
Volumetric data are from Winnick and Powers (1966a).
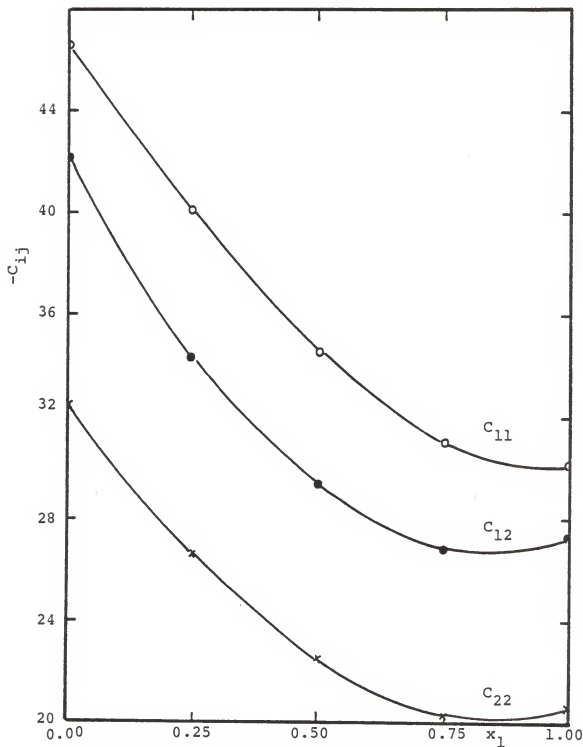
Figure 3-6. DCFI in acetone (1)-carbon disulphide (2) at 273.15 K and 1 atm using the Wilson Equation for excess Gibbs energy.
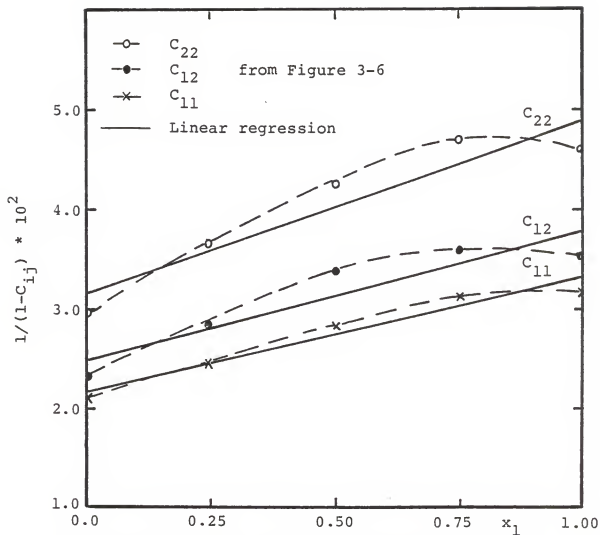
Figure 3-7. Inverse DCFI in acetone (1)-carbon disulphide (2) at 273.15 K and 1 atm using Wilson Equation for excess Gibbs energy.

Table 3-14

Test for Nonideality of Cyclopentane (1)-Cyclooctane (2), P = 1 atm

T, K	x_1	κ, TPa^{-1} x 10^9	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
298.15	0.0	0.803	134.87	32.88	47.26	67.76	67.74
	0.1	0.829	130.79	32.87	47.22	67.72	67.65
	0.2	0.857	126.71	32.86	47.14	67.59	67.44
	0.3	0.888	122.63	32.81	47.01	67.33	67.17
	0.4	0.924	118.57	32.69	46.76	66.89	66.71
	0.5	0.965	114.52	32.48	46.36	66.21	65.99
	0.6	1.014	110.50	32.13	45.76	65.21	64.99
	0.7	1.071	106.50	31.62	44.91	63.84	63.61
	0.8	1.141	102.54	30.90	43.77	62.03	61.83
	0.9	1.226	98.62	29.94	42.27	59.72	59.51
	1.0	1.331	94.73	28.71	40.40	56.87	57.69

$-C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are from Ewing and Marsh (1977).
Activity coefficient data are from Ewing et al. (1970).
Volumetric data are from Ewing et al. (1970).

Table 3-15

Test for Nonideality of Cyclopentane (1)-OMCTS (2), P = 1 atm

T, K	x_1	κ, TP_a^{-1} x10^9	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
298.15	0.0	1.531	312.12	8.89	24.91	82.24	66.88
	0.1	1.523	290.40	9.09	26.83	88.89	76.76
	0.2	1.514	268.67	9.52	29.15	96.71	85.41
	0.3	1.503	246.94	10.16	31.96	106.01	96.34
	0.4	1.490	225.21	11.05	35.37	117.24	108.77
	0.5	1.476	203.47	12.23	39.59	131.07	123.53
	0.6	1.458	181.72	13.77	44.91	148.51	142.70
	0.7	1.436	159.97	15.82	51.82	171.17	164.87
	0.8	1.410	138.21	18.61	61.15	201.82	206.56
	0.9	1.375	116.45	22.60	74.40	245.54	250.55
	1.0	1.331	94.72	28.71	94.69	312.66	307.20

$-C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are from Ewing and Marsh (1977).
Activity coefficient data are from Marsh (1970).
Volumetric data are from Levien and Marsh (1970).

Table 3-16

Test for Nonideality of Methanol (1)-Water (2) at Various Temperatures, P = 1 atm

T, K	x_1	κ, atm^{-1} × 10^4	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
313.00	0.0	0.460	18.16	65.77	31.15	14.38	14.48
	0.2	0.815	22.17	30.89	14.11	6.00	6.16
	0.4	1.049	26.46	21.16	8.92	3.19	3.44
	0.6	1.216	31.16	16.10	6.10	1.56	1.95
	0.8	1.340	36.20	12.71	4.26	0.40	1.01
	1.0	1.437	41.50	10.25	2.93	-1.14	0.37
323.00	0.0	0.463	18.23	63.88	30.12	13.86	13.93
	0.2	0.863	22.31	28.87	12.95	5.41	5.51
	0.4	1.125	26.71	19.42	8.00	2.80	2.97
	0.6	1.311	31.48	14.58	5.40	1.36	1.63
	0.8	1.449	36.59	11.44	3.72	0.36	0.79
	1.0	1.556	42.02	9.19	2.37	-0.93	0.11

-$C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are calculated from Brelvi and O'Connell (1975).
Activity coefficient values are obtained from Van Laar equation.
Parameters are from Hála et al. (1968).
Volumetric data are from Mikhail and Kimel (1961).

Table 3-17

Test for Nonideality of Propanol (1)-Water (2), P = 1 atm

T, K	x_1	κ, atm^{-1} x 10^4	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
313.15	0.0	0.459	18.16	223.83	58.35	14.38	14.67
	0.2	0.777	29.22	94.03	22.32	4.28	4.72
	0.4	0.916	40.81	57.94	13.33	1.88	2.48
	0.6	0.994	52.46	41.74	9.20	0.68	1.43
	0.8	1.044	64.29	32.66	6.49	-0.20	0.67
	1.0	1.078	76.27	26.52	5.05	-0.15	0.33

$C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are calculated from Brelvi and O'Connell (1975).
Activity coefficient values are obtained from Van Laar equation.
Parameters are from Hála et al.(1968).
Volumetric data are from Mikhail and Kimel (1963).

Table 3-18

Test for Nonideality of Acetone (1)-Benzene (2), P = 1 atm

T, K	x_1	κ, atm^{-1} x10^4	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
298.15	0.0	0.960	89.51	22.48	30.02	37.11	39.98
	0.2	1.018	86.18	22.93	29.60	36.26	38.13
	0.4	1.081	82.87	22.95	29.03	35.35	36.65
	0.6	1.149	79.60	22.73	28.37	34.47	35.35
	0.8	1.223	76.35	22.36	27.68	33.51	34.21
	1.0	1.304	73.10	21.91	27.02	32.72	33.27

$C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are calculated from Brelvi and O'Connell (1975).
Activity coefficient values are obtained from Wilson equation.
Parameters are from Prausnitz et al. (1967).
Volumetric data are from Brown and Smith (1962).

Table 3-19

Test for Nonideality of Acetone (1)-Carbontetrachloride (2), P = 1 atm

T, K	x_1	κ, atm^{-1} x10^4	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
298.15	0.0	1.099	97.10	14.84	26.24	35.12	45.84
	0.2	1.131	92.27	18.02	27.13	35.83	40.60
	0.4	1.168	87.40	19.57	27.78	36.49	39.27
	0.6	1.208	82.57	20.60	28.35	37.03	38.88
	0.8	1.253	77.81	21.35	28.82	37.50	38.79
	1.0	1.304	73.10	21.91	29.27	38.03	38.99

$C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are calculated from Brelvi and O'Connell (1975).
Activity coefficient values are obatined from Wilson equation.
Parameters are from Prausnitz et al. (1967).
Volumetric data are from Brown and Smith (1962).

Table 3-20

Test for Nonideality of Nitromethane (1)-Carbon tetrachloride (2) at Various Temperatures, P = 1 atm

T, K	x_1	κ, atm^{-1} x 10^4	V, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
298.15	0.0	1.099	97.10	-8.98	19.56	35.12	---
	0.2	1.051	88.63	8.45	23.08	40.22	60.36
	0.4	0.993	80.02	12.68	26.98	47.09	56.23
	0.6	0.921	71.36	16.58	32.55	56.69	63.03
	0.8	0.829	62.68	21.75	41.03	71.09	76.65
	1.0	0.708	53.95	30.15	55.47	95.12	101.37
303.15	0.0	1.143	97.67	-8.83	18.45	33.25	---
	0.2	1.099	89.17	7.93	21.94	37.93	57.93
	0.4	1.046	80.62	11.99	25.49	43.97	53.02
	0.6	0.980	72.01	15.51	30.38	52.34	57.64
	0.8	0.896	63.35	20.00	37.62	64.54	69.76
	1.0	0.786	54.64	26.94	49.30	83.41	85.99
308.15	0.0	1.172	98.21	-8.43	17.65	32.14	---
	0.2	1.128	89.67	7.60	21.20	36.49	56.31
	0.4	1.075	81.11	11.52	24.58	42.26	51.26
	0.6	1.008	72.45	14.82	29.21	50.38	56.59
	0.8	0.924	63.69	19.10	36.11	62.07	67.51
	1.0	0.813	54.93	25.71	46.89	78.80	84.86

C22,calc is the value obtained using equation (3-19).
Isothermal compressibility data are calculated from Brelvi and O'Connell (1975).
Activity coefficient values are obtained from Wilson equation.
Parameters are from Prausnitz et al. (1967).
Volumetric data are from Gunter et al. (1969).

Table 3-21

Test for Nonideality of Acetonitrile (1)-Carbontetrachloride (2), P = 1 atm

T, K	x_1	κ, atm^{-1} x 10^4	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
298.15	0.0	1.099	97.10	-4.61	18.64	35.12	---
	0.2	1.037	88.20	8.00	22.62	40.95	60.99
	0.4	0.961	79.29	12.51	27.28	48.93	58.19
	0.6	0.867	70.43	17.11	34.09	60.62	66.99
	0.8	0.745	61.64	23.72	45.17	79.75	85.23
	1.0	0.582	52.86	36.12	67.03	117.67	123.68

$C_{22,calc}$ is the value obtained using equation (3-19).

Isothermal compressibility data are calculated from Brelvi and O'Connell (1975).

Activity coefficient values are obtained from Wilson equation.

Parameters are from Prausnitz et al. (1967).

Volumetric data are from Brown and Smith (1962).

Table 3-22

Test for Nonideality of Ethanol (1)-Cyclohexane (2) at Various Temperatures, P = 1 atm

T, K	x_1	κ, atm^{-1} x 10^4	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
298.15	0.0	1.155	108.76	-22.88	21.04	37.49	---
	0.2	1.167	99.18	7.97	23.04	40.72	63.43
	0.4	1.181	89.28	11.25	25.06	44.65	54.44
	0.6	1.199	79.25	13.46	27.69	49.25	55.92
	0.8	1.222	69.11	15.61	31.01	55.00	60.69
	1.0	1.253	58.68	18.14	35.57	62.62	68.87
318.15	0.0	1.360	111.53	-17.76	17.29	30.41	---
	0.2	1.370	101.23	5.76	18.85	33.12	57.29
	0.4	1.383	90.93	8.75	20.51	36.46	46.45
	0.6	1.399	80.62	10.76	22.76	40.31	47.00
	0.8	1.420	70.32	12.67	25.60	45.11	50.76
	1.0	1.447	60.02	14.89	29.56	51.79	57.77

$C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are calculated from Brelvi and O'Connell (1975).
Activity coefficient values are obtained from Wilson equation.
Parameters are from Prausnitz et al. (1967).
Volumetric data are from Pardo and Van Ness (1965).

Table 3-23

Test for Nonideality of Aniline (1)-Benzene (2) at Various Temperatures, P = 1 atm

T, K	x_1	κ, atm⁻¹ x 10⁴	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
298.15	0.0000	1.000	89.40	29.37	36.41	35.54	45.08
	0.4611	0.689	90.12	53.43	52.68	51.39	51.94
	0.7221	0.570	90.70	65.10	63.22	61.18	61.39
	0.8270	0.531	90.99	69.84	67.56	65.21	65.35
	1.0000	0.473	91.53	78.10	75.41	72.75	72.81
308.15	0.000	1.081	90.50	26.12	32.78	32.11	41.07
	0.250	0.927	90.83	37.60	38.27	37.43	38.95
	0.500	0.774	91.13	46.17	45.67	44.67	45.17
	0.750	0.623	91.61	57.87	56.40	54.77	56.93
	1.000	0.474	92.31	76.06	73.44	73.83	70.90
318.15	0.000	1.134	93.42	24.36	30.56	29.95	38.27
	0.250	0.973	92.36	34.69	35.58	34.95	36.49
	0.500	0.814	92.60	42.72	42.49	41.72	42.26
	0.750	0.655	92.99	53.66	52.48	51.10	51.32
	1.000	0.498	90.25	70.60	68.40	66.17	66.27

$C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are from Gibson and Loeffler (1939a).
Activity coefficient values are obtained from Wilson equation.
Parameters are evaluated from Martin and Collie (1932).
Volumetric data are from Deshpande and Bhatgade (1968).

Table 3-24

Test for Nonideality of Aniline (1)-Chlorobenzene (2) at Various Temperatures, P = 1 atm

T, K	x_1	κ, atm^{-1} x 10^4	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
298.15	0.0	0.709	102.23	-17.26	52.10	57.94	---
	0.2	0.662	100.18	48.57	57.53	63.31	68.11
	0.4	0.613	98.08	55.62	63.20	69.99	71.79
	0.6	0.561	95.92	62.53	70.43	78.38	79.31
	0.8	0.508	93.73	70.96	79.72	89.00	89.55
	1.0	0.451	91.53	81.90	91.84	102.64	102.97
308.15	0.0	0.757	103.27	-14.42	47.28	52.98	---
	0.2	0.705	101.13	44.16	52.70	57.98	62.85
	0.4	0.651	99.01	51.00	58.06	64.23	66.08
	0.6	0.595	96.82	57.49	64.89	72.26	73.23
	0.8	0.536	94.57	65.50	73.80	82.56	83.13
	1.0	0.474	92.31	76.06	85.39	95.48	95.85
318.15	0.0	0.807	104.30	-12.15	43.07	48.53	---
	0.2	0.750	102.10	40.25	48.38	53.17	58.11
	0.4	0.692	99.96	46.80	53.40	59.01	60.91
	0.6	0.630	97.74	52.87	59.83	66.69	67.69
	0.8	0.566	95.42	60.46	68.32	76.59	77.18
	1.0	0.498	93.10	70.60	79.28	88.64	89.01

$C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are calculated from Brelvi and O'Connell (1975).
Activity coefficient values are obtained from Wilson equation.
Parameters are evaluated from Coulter et al. (1941).
Volumetric data are from Deshpande and Bhatgadde (1968).

Table 3-25

Test for Nonideality of Chloroform (1)-Ethyl Ether (2), P = 1 atm

T, K	x_1	κ, atm^{-1} × 10^4	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
298.15	0.0000	1.970	104.69	9.97	14.73	20.73	21.55
	0.1256	1.680	101.12	12.80	18.38	25.34	26.22
	0.2442	1.500	97.89	15.53	21.72	29.31	30.23
	0.3566	1.370	94.98	18.22	24.89	32.88	33.87
	0.5639	1.180	90.03	23.57	30.94	39.35	40.52
	0.6698	1.105	87.70	26.31	33.96	42.46	43.75
	0.7511	1.065	85.99	28.09	35.90	44.32	45.81
	0.8380	1.035	84.21	29.69	37.62	45.90	47.60
	1.0000	0.990	80.97	32.44	40.70	45.54	51.00

$C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are from Dolezalek and Speidel (1920).
Activity coefficient values are obtained from solubility parameter theory.
Volumetric data are from Beath et al. (1969).

Table 3-26

Test for Nonideality of Ethanol (1)-Water (2), P = 1 atm

T, K	x_1	κ, atm^{-1} x 10^4	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
313.12	0.0	0.460	18.16	127.21	44.15	14.35	14.90
	0.2	0.732	25.64	64.76	20.46	5.47	6.00
	0.4	1.009	33.72	37.62	10.90	2.12	2.67
	0.6	1.213	42.12	25.46	6.74	0.69	1.26
	0.8	1.330	50.74	19.39	4.53	-0.10	---
	1.0	1.394	59.67	15.66	2.88	-0.33	---

$C_{22,calc}$ is the value obtained by using equation (3-19).
Isothermal compressibility data are calculated from Brelvi and O'Connell (1975).
Activity coefficient values are obtained from Van Laar equation.
Parameters are from Hála et al. (1968).
Volumetric data are from Bearce et al. (1928).

Table 3-27

Test for Nonideality of Acetone (1)-Water (2), P = 1 atm

T, K	x_1	κ, atm^{-1} x10^4	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
298.15	0.0	0.462	18.07	210.61	57.44	14.98	15.14
	0.2	0.812	28.21	87.98	21.48	4.38	4.68
	0.4	1.218	39.55	46.61	9.43	0.79	1.28
	0.6	1.669	52.07	27.44	4.18	-0.81	---
	0.8	2.077	65.46	17.76	1.82	-1.66	---
	1.0	2.293	79.17	13.11	0.97	-2.01	---

$C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are calculated from Brelvi and O'Connell (1975).
Activity coefficient values are obtained from Van Laar equation.
Parameters are from Hála et al. (1968).
Volumetric data are from Bearce et al. (1928).

Table 3-28

Test for Nonideality of Benzene (1)-Dichloroethylene (2) at Various Temperatures, P = 1 atm

T, K	x_1	κ, atm^{-1} x 10^{-4}	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
293.12	0.0	0.793	77.37	53.95	46.28	39.57	39.68
	0.2	0.840	79.85	48.62	42.00	36.16	36.26
	0.4	0.867	82.23	45.37	39.39	34.07	34.18
	0.6	0.894	84.52	42.59	37.12	32.23	32.34
	0.8	0.924	86.73	40.00	35.01	30.52	30.63
	1.0	0.968	88.86	37.17	32.71	28.68	28.77
313.12	0.0	0.922	79.22	44.09	37.89	32.44	32.54
	0.2	0.976	81.75	39.94	34.48	29.64	29.65
	0.4	1.020	84.20	36.84	31.92	27.54	27.64
	0.6	1.049	86.57	34.66	30.14	26.09	26.19
	0.8	1.079	88.87	32.70	28.55	24.81	24.91
	1.0	1.120	91.08	30.65	26.89	23.48	23.58

C_{22},calc is the value obtained using equation (3-19).
Isothermal compressibility data are from Staveley et al. (1955).
Activity coefficient values are obtained from solubility parameter theory.
Volumetric data are from Findenegg and Kohler (1969).

Table 3-29

Test for Nonideality of Aniline (1)-Nitrobenzene (2) at Various Temperatures, P = 1 atm

T, K	x_1	κ, atm^{-1} x 10^{-4}	v, cc/mol	$-C_{11}$	$-C_{12}$	$-C_{22}$	$-C_{22,calc}$
338.15	0.0000	0.623	106.16	49.41	54.73	60.42	60.61
	0.1668	0.622	104.45	49.55	54.34	61.60	59.58
	0.3051	0.619	102.93	50.15	56.28	62.96	63.14
	0.4312	0.626	101.50	50.07	56.37	63.29	63.45
	0.6842	0.603	98.51	54.41	60.37	68.07	68.22
	0.7984	0.597	97.12	54.70	61.90	69.88	70.03
	0.8909	0.593	95.99	55.72	63.10	71.30	71.44
	1.0000	0.584	94.65	57.41	65.06	73.59	73.71
358.15	0.0000	0.699	108.02	42.91	47.23	51.59	51.97
	0.1668	0.697	106.07	42.26	47.33	52.70	52.99
	0.3051	0.693	104.46	42.72	48.13	53.98	54.21
	0.4312	0.709	102.99	42.26	47.67	53.58	53.76
	0.6842	0.670	100.04	46.17	52.03	58.49	58.62
	0.7984	0.670	98.71	46.78	52.81	59.49	59.60
	0.8909	0.670	97.64	47.28	53.57	60.58	60.68
	1.0000	0.656	96.36	48.99	55.95	63.84	63.88

$C_{22,calc}$ is the value obtained using equation (3-19).
Isothermal compressibility data are from Gibson and Loeffler (1939b).
Activity coefficient values are obtained from Van Laar equation.
Parameters are evaluated from Holtzlander and Riggle (1955).
Volumetric data are calculated from Brelvi and O'Connell (1975).

$$g^E = \frac{G^E}{RT}$$

$$= x_1 \, x_2 \, A \tag{3-24}$$

From equation (3-24) and using thermodynamic relations we can get expressions for excess entropy, excess enthalpy, and excess volume as given by

$$s^E = -x_1 \, x_2 \, \frac{\partial A}{\partial T} \bigg|_P \tag{3-25}$$

$$h^E = x_1 \, x_2 \, \frac{\partial A/T}{\partial 1/T} \bigg|_P \tag{3-26}$$

$$v^E = x_1 \, x_2 \, \frac{\partial A}{\partial P} \bigg|_T \tag{3-27}$$

Assuming some form for A such as

$$A = A_o + A_p P + A_t T \tag{3-28}$$

where A_o, A_p, and A_t are constants, we get for thermodynamic properties the following:

$$s^E = -x_1 \, x_2 \, A_t \tag{3-29}$$

$$v^E = x_1 \, x_2 \, A_p \tag{3-30}$$

$$h^E = x_1 \, x_2 \, [A_o + A_p \, P] \tag{3-31}$$

$$h^E = x_1 x_2 A_o + v^E P \tag{3-32}$$

$$u^E = x_1 x_2 A_o \tag{3-33}$$

$$\kappa v = x_1 v_1^o \kappa_1^o + x_2 v_2^o \kappa_2^o \tag{3-34}$$

$$\overline{v}_i = v_i^o + A_p x_j^2 \tag{3-35}$$

$$\ln \gamma_i = A x_j^2 \tag{3-36}$$

$$\frac{d \ln \gamma_i}{d x_i} = -2A x_j \tag{3-37}$$

In order to simplify further our equations, we assume that A is a constant independent of pressure and temperature; then for a regular quadratic mixture (regular because excess entropy is zero, quadratic because Gibbs energy is quadratic in mole fraction), the direct correlation function integrals are

$$(1 - C_{11}) = \frac{v_1^{o^2}}{RT(x_1 v_1^o \kappa_1^o + x_2 v_2^o \kappa_2^o)} - 2A x_2^2 \tag{3-38}$$

$$(1 - C_{12}) = \frac{v_1^o v_2^o}{RT(x_1 v_1^o \kappa_1^o + x_2 v_2^o \kappa_2^o)} + 2A x_1 x_2 \tag{3-39}$$

$$(1 - C_{22}) = \frac{v_2^{o^2}}{RT(x_1 v_1^o \kappa_1^o + x_2 v_2^o \kappa_2^o)} - 2A x_1^2 \tag{3-40}$$

In the particular case of infinite dilution equations (3-38) to (3-40) reduce to

$$(1 - C_{11})^{\infty 1} = \frac{v_1^{o^2}}{RT \; v_2^o \; \kappa_2^o} - 2A \tag{3-41}$$

$$(1 - C_{12})^{\infty 1} = \frac{v_1^o}{RT \; \kappa_2^o} \tag{3-42}$$

$$(1 - C_{22})^{\infty 1} = \frac{v_2^o}{RT \; \kappa_2^o} \tag{3-43}$$

where the superscript $\infty 1$ indicates that mole fraction of component one goes to zero.

$$(1 - C_{11})^{\infty 2} = \frac{v_1^o}{RT \; \kappa_1^o} \tag{3-44}$$

$$(1 - C_{12})^{\infty 2} = \frac{v_2^o}{RT \; \kappa_2^o} \tag{3-45}$$

$$(1 - C_{22})^{\infty 2} = \frac{v_2^{o^2}}{RT \; v_1^o \; \kappa_1^o} - 2A \tag{3-46}$$

where the superscript $\infty 2$ indicates that mole fraction of component two goes to zero.

To test if a solution modeled by the Margules equation could show maxima and crossing of the C_{ij}, we apply these equations to the acetone-carbon disulphide system. A crossing of the C_{ij} exists only if the unrealistic value

of 4.45 is used for A (a value of 1 for A indicates the limit of inmiscibility). Further, no maximum can be found for C_{11} at zero acetone mole fraction, unless A is of the order of 5.00 E13.

Another empirical equation for excess Gibbs free energy (Abott and Van Ness, 1975) is given by

$$\frac{g^E}{x_1 \, x_2} = A_{21} \, x_1 + A_{12} \, x_2 - (\lambda_{21} \, x_1 + \lambda_{12} \, x_2) \, x_1 \, x_2$$

$$(3-47)$$

This equation with its four constants related to infinite dilution behavior allows more variation in the behavior of direct correlation function integrals. The four parameters in equation (3-47) are given by

$$A_{12} = \ln \gamma_1^{\infty 1} \qquad (3-48)$$

$$A_{21} = \ln \gamma_2^{\infty 2} \qquad (3-49)$$

$$\lambda_{12} = A_{21} - 2A_{12} - \frac{1}{2} \frac{d \ln \gamma_1}{dx_1} \bigg|^{\infty 1} \qquad (3-50)$$

$$\lambda_{21} = A_{12} - 2A_{21} - \frac{1}{2} \frac{d \ln \gamma_2}{dx_2} \bigg|^{\infty 2} \qquad (3-51)$$

Table 3-30 presents values for the partial derivative of activity coefficient for the acetone-carbon disulphide system with various sets of infinite dilution values in

Table 3-30

Derivatives of Activity Coefficients for Acetone (1)-Carbon Disulphide (2), P = 1 atm

x_1	From the Equations of Winnick and Powers (1966b)		From Equation (3-47) with Infinite Dilution Values from Winnick and Powers	
	$d\ln\gamma_1/dx_1$	$d\ln\gamma_2/dx_2$	$d\ln\gamma_1/dx_1$	$d\ln\gamma_2/dx_2$
0.0	-14.32	0.00	-14.32	0.00
0.1	-7.48	-0.83	-9.13	-0.61
0.2	-4.06	-1.01	-5.30	-1.32
0.3	-2.60	-1.11	-2.68	-1.15
0.4	-2.05	-1.36	-1.12	-0.75
0.5	-1.73	-1.73	-0.39	-0.39
0.6	-1.34	-2.02	-0.27	-0.41
0.7	-0.88	-2.06	-0.49	-1.14
0.8	-0.53	-2.13	-0.74	-2.96
0.9	-0.42	-3.75	-0.70	-6.28
1.0	0.00	-11.54	0.00	-11.54

x_1	From Equation (3-47) with $\left.\frac{d\ln\gamma_1}{dx_1}\right\|_{\infty 1}=-12.0$ and $\left.\frac{d\ln\gamma_2}{dx_2}\right\|_{\infty 2}=-11.54$		From Equation (3-47) with $\left.\frac{d\ln\gamma_1}{dx_1}\right\|_{\infty 1}=-12.0$ and $\left.\frac{d\ln\gamma_2}{dx_2}\right\|_{\infty 2}=-6.0$	
	$d\ln\gamma_1/dx_1$	$d\ln\gamma_2/dx_2$	$d\ln\gamma_1/dx_1$	$d\ln\gamma_2/dx_2$
0.0	-12.00	0.00	-12.00	0.00
0.1	-8.57	0.95	-7.62	0.85
0.2	-5.60	1.40	-4.71	1.18
0.3	-3.25	1.40	-2.91	1.24
0.4	-1.62	1.08	-1.89	1.26
0.5	-0.68	0.68	-1.38	1.38
0.6	-0.35	0.52	-1.14	1.72
0.7	-0.42	0.99	-1.01	2.35
0.8	-0.65	2.58	-0.82	3.29
0.9	-0.65	5.88	-0.50	4.53
1.0	0.00	-11.54	0.00	6.00

equations (3-4) to (3-51). Figure 3-8 shows C_{11} values over the entire concentration range for the original Winnick and Powers values and for the arbitrarily chosen infinite dilution derivatives. Figure 3-9 shows the dilute acetone ($x_1 \to 0$) behavior of C_{11} for all values used in Table 3-30. Finally, Figure 3-10 presents the shape of the excess Gibbs free energy for each set given in Table 3-30.

In conclusion we can say that simple forms of C_{ij} reproduce very well the excess Gibbs free energy calculated with complicated forms of C_{ij}. In other words, the figures indicate that modelling the C_{ij} would be desirable for predicting g^E values because results are not extremely sensitive to C_{ij} values, particularly at high dilutions. On the other hand, the same insensitivity indicates that the "experimental" direct correlation function integrals are uncertain. This uncertainty in the C_{ij} is a major obstacle to modelling.
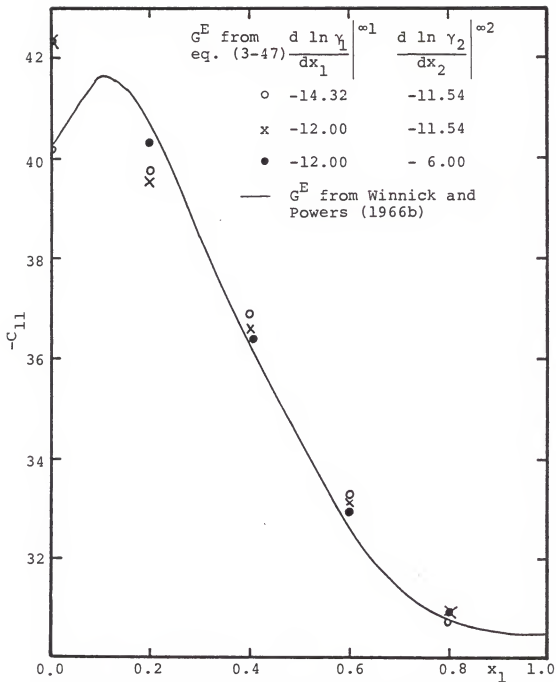
Figure 3-8. $-C_{11}$ for acetone (1) in carbon disulphide at 273.15 K and 1 atm from various expressions for G^E.
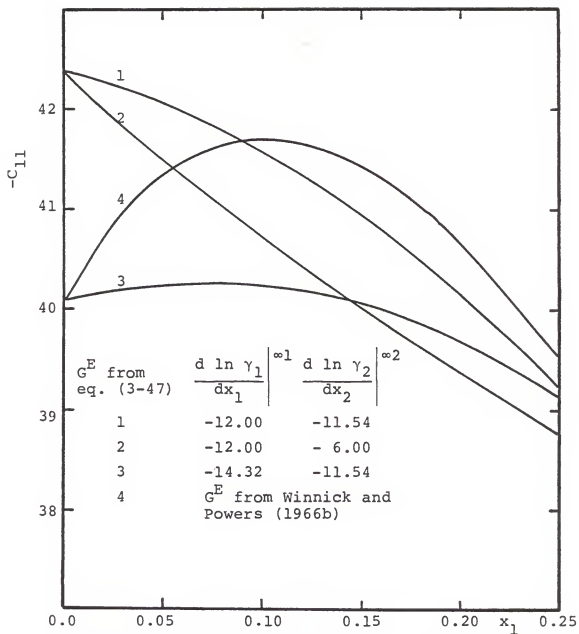
Figure 3-9. $-C_{11}$ for acetone (1) in carbon disulphide at 273.15 K and 1 atm from various expressions for G^E.
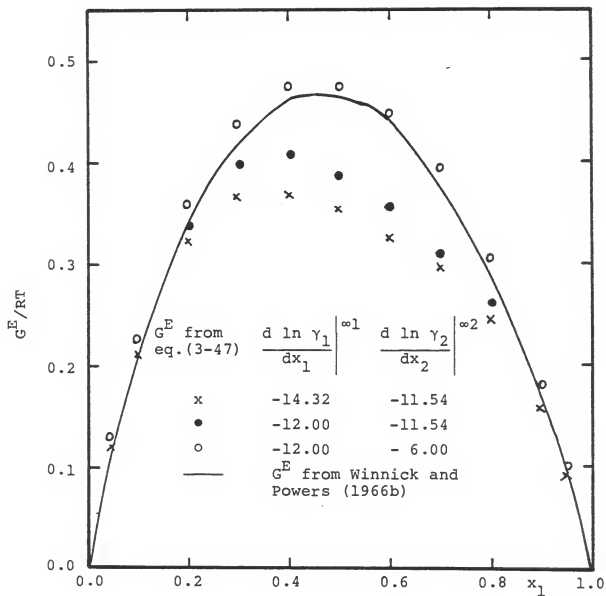
Figure 3-10. Excess Gibbs energies for acetone (1) and carbon disulphide at 273.15 K and 1 atm from various expressions.

CHAPTER 4
MODELS FOR DIRECT CORRELATION FUNCTION INTEGRALS

4.1   Introduction

In order to be applied, the fluctuation solution theory presented in Chapter 2 requires a model for the direct correlation function integrals. This chapter describes experience with one such model. Its concept is that condensed fluid behavior can be expressed as that of a hard sphere fluid plus a perturbation. Here, the equation for the direct correlation function integrals is a hard sphere expression plus a linear density term. Section 4.2 describes this idea as used by Mathias (1978) for gas solubility. Section 4.3 introduces a modification in the hard sphere expression to more closely describe pure liquid compressions. Section 4.4 investigates the possibility of replacing the hard sphere equation with a hard convex expression. Finally, Section 4.5 shows application of the Mathias model to solubilities of gases in binary solvents.

4.2   Description of the Basic Model

The basis of the present model for direct correlation function integrals comes from work by Mathias (1978, 1981). We will describe its physical picture, generalize its

equations, present its extension to multicomponent systems, and explain its working procedure.

In the early 1970s, it was shown that the structure of a simple pure fluid is basically the structure of an equivalent hard sphere fluid (Chandler et al., 1983). Intermolecular forces are separated into short-range repulsion and long-range attraction. At high densities the structure of liquids is determined by packing effects related to the short-range repulsion. On the other hand, the long-range attraction generates a uniform background potential that keeps the liquids at its high density but does not affect the structure.

For hard spheres, analytical expressions such as the Percus-Yevick compressibility equation (Lebowitz and Rowlinson, 1964) give accurate compressibility factors at densities up to three-fourths of that of the solid-liquid transition. For higher densities, the semiempirical expressions such as Carnahan-Starling (1969) equation are better. As a result, the thermodynamic properties of hard-sphere fluids are well described over the full range of density.

The properties of real spherical liquids may be calculated by a perturbation technique with the hard sphere as a reference and with the attractive forces as a perturbation. For the direct correlation function integral of a pure liquid the simplest expression of this physical

picture means a hard sphere expression plus a linear density correction term

$$C(T,\rho) = C^{hs}(\tilde{\rho}) + \rho\ B(T) \qquad (4-1)$$

where $\tilde{\rho}$ is the density reduced by a suitable spherical covolume.

Before giving particular functional forms and variables in equation (4-1), it should be noted that Gubbins and O'Connell (1974) and Brelvi and O'Connell (1972) showed that a corresponding states behavior can be found for the direct correlation function integrals of pure components. Figure 4-1 shows the generalized correlation for C of Brelvi and O'Connell (1972). The correlation works quite well for densities larger than 1.5 $\rho*$, where $\rho*$ is a characteristic parameter close to the critical density for nonpolar substances but larger for polar species. Mathias (1978) introduced a two parameter corresponding states correlation in the form of equation (4-1).

$$C(T,\rho) = C^{hs}(\tilde{\rho},\tilde{T}) - 2\ \tilde{\rho}[g(\tilde{T}) - f(\tilde{T})] \qquad (4-2)$$

with

$$C^{hs}(\tilde{\rho},\tilde{T}) = \Phi(\eta) = \Phi[\frac{\tilde{\rho}}{4}\ f(\tilde{T})] \qquad (4-3a)$$

where the hat ~ indicates reduced property, and η is the packing fraction, here a function of reduced temperature
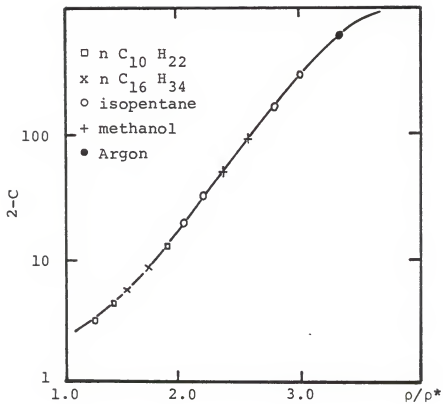
Figure 4-1. Generalized correlation for
pure component DCFI with re-
duced density (Brelvi and
O'Connell, 1972).

and density. Equation (4-2) uses two parameters, a charac-
teristic temperature, T^*, and a characteristic volume, V^*,
or density, ρ^*. The two functions f and g were determined
by Mathias from data on pure argon. Appendix A presents a
complete list of his equations and functions.

Introducing equation (4-2) in equation (2-29) we ob-
tain the following equation of state for a pure liquid phase

$$\frac{p^f - p^r}{RT} = \rho^f (1 + \eta_f^4 - 2\eta_f^3)/(1 - \eta_f)^4$$

$$- \rho^r (1 + \eta_r^4 - 2\eta_r^3)/(1 - \eta_r)^4$$

$$+ (\rho_f^2 - \rho_r^2) \, V^* \, (g(T/T^*) - f(T/T^*)) \quad (4-4)$$

where

$$\eta = \frac{\rho V^*}{4} \, f(T/T^*) \tag{4-5}$$

The correlation of pure compression data is generally
good, with the results being sensitive to the value of V^*
but insensitive to T^*. As our objective is to work with
mixtures, the main use of equation (4-4) is only to obtain
pure component parameters.

For mixtures it is assumed that the pair direct cor-
relation function integrals are given by an extension of
equation (4-2)

$$C_{ij}(T,\rho) = c_{ij}^{hs} - 2\rho V_{ij}^* [g_{ij} - f_{ij}] \qquad (4\text{-}6)$$

with

$$c_{ij}^{hs} = \phi(\underline{\xi}) \qquad (4\text{-}7)$$

where

$$\xi_k = \frac{\pi}{6} \sum_{i=1}^{n} \rho_i \left(\frac{3}{2} \frac{V_{ii}^* f_i}{\pi}\right)^{k/3} \quad k = 0, 1, 2, 3 \qquad (4\text{-}8)$$

and

$$f_i = f(T/T_{ii}^*) \qquad (4\text{-}9a)$$

in addition

$$g_{ij} = g(T/T_{ij}^*) \qquad (4\text{-}9b)$$

and

$$f_{ij} = \left(\frac{f_i^{1/3} + f_j^{1/3}}{2}\right)^3 \qquad (4\text{-}9c)$$

In previous work (Mathias, 1978), the hard sphere mixture direct correlation function integral, c_{ij}^{hs}, is described by the Carnahan-Starling equation for mixtures. Mixing rules are required for evaluating the characteristic parameters, V_{ij}^* and T_{ij}^* for $i \neq j$. The mixing rules used are

$$V_{ij}^* = \frac{1}{8} \left(V_{ii}^{*1/3} + V_{jj}^{*1/3}\right)^3 \qquad (4\text{-}10)$$

where V_{ii}^* is the characteristic volume for pure i

$$T_{ij}^* = (T_{ii}^* \, T_{jj}^*)^{1/2} \, (1 - k_{ij}) \qquad (4-11)$$

where T_{ii}^* is the characteristic temperature for pure i, and k_{ij} is the binary parameter which must be evaluated from binary data.

Introducing equation (4-6) in equation (2-29), we obtain the following equation of state for a multicomponent liquid phase

$$\frac{P^f - P^r}{RT} = \frac{P^{hs}(T, \underline{\rho}^f)}{RT} - \frac{P^{hs}(T, \underline{\rho}^r)}{RT}$$

$$+ \sum_{i=1}^{n} \sum_{j=1}^{n} [\rho_i^f \rho_j^f - \rho_i^r \rho_j^r] \, V_{ij}^* \, (g_{ij} - f_{ij})$$

$$(4-12)$$

Similarly, introducing equation (4-6) in equation (2-30) we can obtain an expression for activity coefficients of multicomponent liquid mixtures (see Appendix A for details).

4.3 Comparison of Different Hard Sphere Equations

Mathias (1978) used the Carnahan-Starling equation for the reference term because it is the best analytic expression for hard spheres. This fixed the reference term in equation (4-1), and he found a functional form for the hard sphere diameter and the linear density coefficient from

compression data on argon, the reference compound. An alternative to his procedure is to keep free the reference equation. Telotte and O'Connell (1982) used this approach in fitting pure component data to a generalized hard sphere equation of state

$$z^{hs} = \frac{1 + \eta + \eta^2 + \alpha\eta^3}{(1 - \eta)^3} \qquad (4-13)$$

or its pressure equivalent

$$P^{hs} = RT\rho \frac{(1 + \eta + \eta^2 + \alpha\eta^3)}{(1 - \eta)^3} \qquad (4-14)$$

or

$$C^{hs} (\tilde{\rho}, \tilde{T}, \alpha) = \Phi(\eta, \alpha) \qquad (4-3b)$$

where α is a parameter, and it is related with the steepness of isotherms in the P-ρ diagram. Different choices of α yield different hard sphere equations. The Carnahan-Starling expression results from a value of $\alpha = -1$, the Percus-Yevick compressibility equation from a values of $\alpha = -3$, and the Percus-Yevick virial equation from $\alpha = 0$.

Telotte's approach was to treat α as adjustable parameter in the building of the model. He chose methane as the reference. Minimizing the difference between the experimental direct correlation function integral given

by equation (4-2) with C from equation (4-3b), an optimum value of -4.2 was found for α.

The choice of hard sphere equations to use as a reference is critical not only for pure components, but also in mixtures. Equations with the adjustable parameter α for mixture pressure and direct correlation function integrals in a multicomponent mixture are presented in Appendix B. We describe our analysis with the n-heptane--n-octane system (ideal mixture) and with acetone-carbon disulphide system (nonideal mixture) to determine the sensitivity of the composition dependence. A simple way to do this is to evaluate the hard sphere diameter for each component when pure. At fixed α the diameter is calculated by taking the hard sphere direct correlation function integral equal to the corresponding experimental value. Then the differences between the experimental data and the calculated values using equation (B-6) are examined over the entire concentration range. Table 4-1 presents results for n-heptane with n-octane at constant pressure. The B_{ij} column is the difference between the experimental and the calculated C_{ij} divided by the solution density. Figure 4-2 displays the experimental and the calculated direct correlation function integrals for the pairs of n-heptane. The small influence of varying the α value is clear from the figure. The same is true for the other direct correlation function integrals in Table 4-1. Further, while the value of B_{ij} varies strongly with composition in all cases, the value

Table 4-1

Direct Correlation Function Integrals Comparison Using Different α in n-heptane (1)--n-Octane (2), T = 333.15 K, P = 1 atm

α	x	$-C_{11}$	B_{11}	$-C_{12}$	B_{12}	$-C_{22}$	B_{22}
0.0	0.0000	29.52	-277.84	33.88	-157.78	38.87	0.00
	0.1727	29.41	-222.80	33.74	-101.08	38.70	58.17
	0.3463	29.29	-157.71	33.59	- 32.74	38.52	129.11
	0.5870	29.12	- 88.19	33.39	38.58	38.28	201.69
	0.7796	28.97	- 42.43	33.21	84.97	38.06	247.67
	1.0000	28.80	0.00	33.01	126.86	37.82	288.24
-1.0	0.0000	29.51	-280.06	33.87	-159.02	38.87	0.00
	0.1727	29.40	-224.76	33.74	-102.05	38.70	58.37
	0.3463	29.28	-159.35	33.59	- 33.38	38.52	129.66
	0.5870	29.11	- 89.33	33.39	38.48	38.29	202.81
	0.7796	28.96	- 43.06	33.21	85.41	38.07	249.37
	1.0000	28.80	0.00	33.01	127.97	37.83	290.67
-3.0	0.0000	29.43	-294.40	33.83	-166.96	38.87	0.00
	0.1727	29.33	-236.50	33.71	-107.10	38.72	61.62
	0.3463	29.22	-168.47	33.58	- 35.53	38.56	136.14
	0.5870	29.08	- 95.04	33.40	40.10	38.35	213.48
	0.7796	28.95	- 46.03	33.24	90.06	38.16	263.42
	1.0000	28.80	0.00	33.06	135.88	37.95	308.33

$B_{ij} = (C_{ij}^{exp} - C_{ij})/\rho$. C_{ij}^{exp} are from Table (3-1) and C_{ij} are calculated using the hard-sphere equation (B-6).

Figure 4-2. Isobaric (1 atm) $-c_{11}$ values in n-heptane (1)--n-octane at 333.15 K.

of c_{ij}^{hs} does not. Therefore, the compositional variation in mixtures must be correlated differently than these of pure fluids.

Table 4-2 presents results for n-heptane--n-octane at a constant density and Figure 4-3 shows direct correlation function integrals for the n-heptane--n-heptane pair. Again, there is only a small difference between the numbers from the different hard sphere equations.

Similar results for the system acetone-carbon disulphide are presented in Tables 4-3, 4-4 and Figures 4-4, 4-5.

4.4 Hard Convex Body as Reference

Complex molecules have nonspherical hard cores. For modelling of direct correlation function integrals we investigate the possibility of using an equation for a convex body of revolution.

The direct correlation function integral for hard convex body is obtained in this work from Boublik's compressibility factor equation (Boublik, 1975)

$$z = \frac{1 + (3\gamma - 2)\ \eta + (3\gamma^2 - 3\gamma + 1)\ \eta^2 - \gamma^2 \eta^3}{(1 - \eta)^3} \qquad (4-15)$$

where z, the compressibility factor is

$$z = \frac{P}{RT\rho} \qquad (4-16)$$

Table 4-2

Direct Correlation Function Integrals Comparison Using Different α
in n-Heptane (1)--n-Octane (2), T - 333.15 K, V = 135.37 cc/mol

α	x	$-C_{11}$	B_{11}	$-C_{12}$	B_{12}	$-C_{22}$	B_{22}
0.0	0.00	173.54	-672.30	200.25	-438.38	231.06	0.00
	0.25	139.41	-1397.54	160.60	-1359.12	185.00	-1189.54
	0.50	113.60	-1325.55	130.66	-1355.41	150.26	-1301.49
	0.75	93.76	-785.27	107.67	-803.19	123.62	-764.24
	1.00	78.28	0.00	89.75	45.86	102.88	134.73
-1.0	0.00	173.74	-646.11	200.37	-422.86	231.06	0.00
	0.25	139.31	-1410.39	160.39	-1387.50	184.65	-1236.39
	0.50	113.45	-1345.42	130.40	-1389.85	149.87	-1354.52
	0.75	93.67	-797.86	107.48	-827.81	123.33	-804.27
	1.00	78.28	0.00	89.68	37.04	102.73	114.36
-3.0	0.00	172.51	-811.79	199.66	-518.30	231.06	0.00
	0.25	138.01	-1559.90	159.66	-1486.57	184.42	-1268.65
	0.50	112.70	-1446.68	129.96	-1449.63	149.84	-1358.90
	0.75	93.31	-845.72	107.41	-837.56	123.62	-764.18
	1.00	78.28	0.00	89.96	73.95	103.35	198.18

$B_{ij} = (C_{ij}^{exp} - C_{ij})/\rho$. C_{ij} are calculated using the hard-sphere equation (B-6).
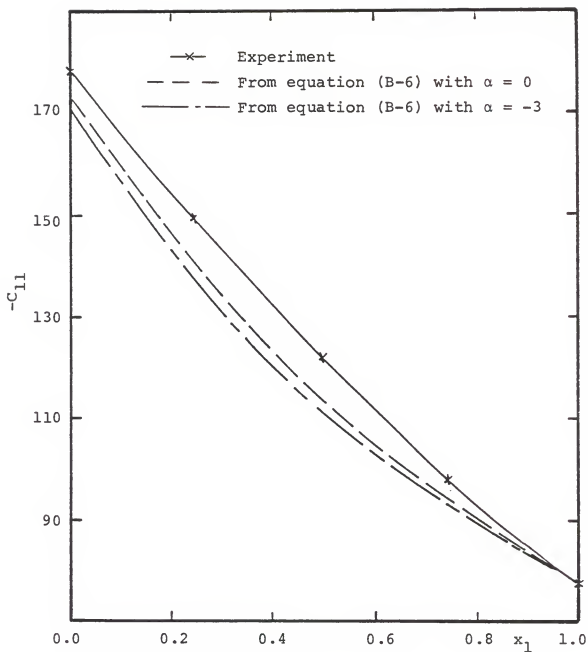
Figure 4-3. Isochoric (135.37 cc/mol) $-C_{11}$ values in n-heptane (1)--n-octane at 333.15 K.

Table 4-3

Direct Correlation Function Integrals Comparison Using Different α in Acetone (1)-Carbon Disulphide (2), $T = 273.15$ K, $P = 1$ atm

α	x	$-C_{11}$	B_{11}	$-C_{12}$	B_{12}	$-C_{22}$	B_{22}
0.0	.00	42.72	-226.18	37.25	-285.04	32.47	0.00
	.25	37.11	-182.27	32.39	-125.05	28.27	107.99
	.50	33.48	- 69.66	29.25	- 14.29	25.55	199.97
	.75	31.11	1.21	27.19	22.47	23.76	240.04
	1.00	30.31	0.00	26.49	60.39	23.15	172.97
-1.0	.00	42.67	-229.24	37.23	-286.38	32.47	0.00
	.25	37.09	-182.97	32.40	-124.41	28.29	109.62
	.50	33.49	- 69.20	29.28	- 12.67	25.58	202.42
	.75	31.12	0.36	27.22	24.42	23.80	242.77
	1.00	30.31	0.00	26.51	59.14	23.18	175.10
-3.0	.00	42.28	-252.25	36.91	-304.77	32.22	- 14.73
	.25	36.94	-192.47	32.29	-131.14	28.22	104.97
	.50	33.46	- 71.35	29.27	- 13.03	25.60	203.28
	.75	31.15	1.14	27.26	27.23	23.85	246.41
	1.00	30.31	0.00	26.53	57.57	23.22	177.72

$B_{ij} = (C_{ij}^{exp} - C_{ij})/\rho$. C_{ij}^{exp} are from Table (3-13) and C_{ij} are calculated using the hard-sphere equation (B-6).

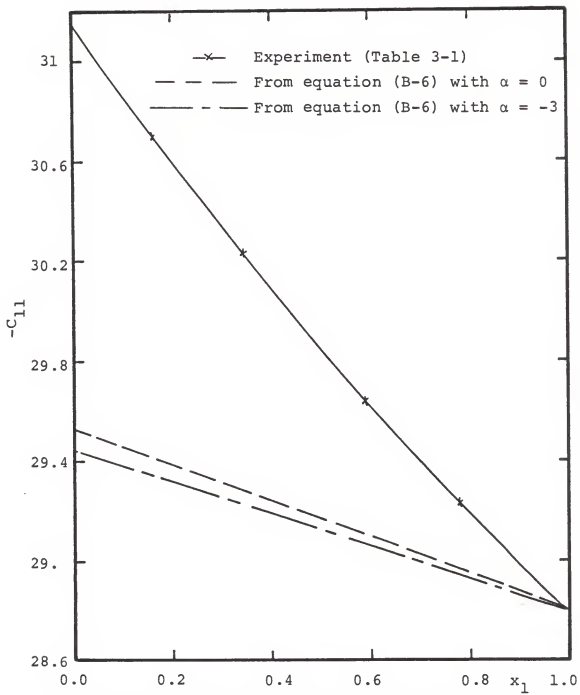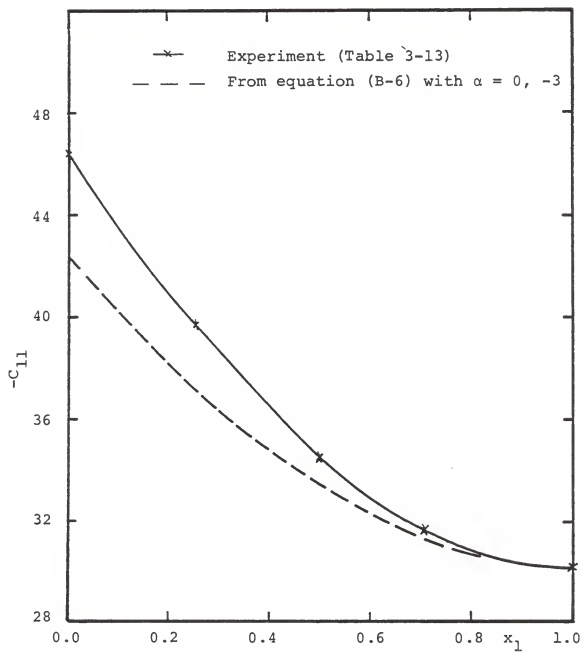Figure 4-4. Isobaric (1 atm) $-C_{11}$ values in acetone (1)-carbon disulphide at 273.15 K.

Table 4-4

Direct Correlation Function Integrals Comparison Using Different α
in Acetone (1)-Carbon Disulphide (2), T = 273.15 K, V = 58.67 cc/mol

α	x	$-C_{11}$	B_{11}	$-C_{12}$	B_{12}	$-C_{22}$	B_{22}
0.0	.00	51.36	285.12	40.83	− 71.77	32.43	0.00
	.25	65.30	−229.47	51.67	− 442.28	40.86	− 377.04
	.50	84.81	−597.78	66.80	− 822.98	52.59	− 737.30
	.75	112.90	−806.00	88.51	−1184.29	69.37	−1047.91
	1.00	154.69	0.00	120.70	−1102.85	94.16	−1081.38
−1.0	.00	51.40	287.47	40.84	− 70.77	32.43	0.00
	.25	65.20	−235.03	51.57	− 447.98	40.77	− 382.68
	.50	84.58	−611.32	66.58	− 835.74	52.39	− 749.13
	.75	112.62	−822.50	88.23	−1200.82	69.10	−1063.82
	1.00	154.69	0.00	120.59	−1109.25	93.98	−1091.50
−3.0	.00	52.23	336.04	41.18	− 51.22	32.43	0.00
	.25	65.86	−196.34	51.68	− 441.69	40.52	− 397.38
	.50	84.97	−588.12	66.35	− 849.59	51.77	− 785.78
	.75	112.71	−817.37	87.55	−1240.90	67.96	−1130.27
	1.00	154.69	0.00	119.51	−1172.62	92.29	−1190.94

$B_{ij} = (C_{ij}^{exp} - C_{ij})/\rho$. C_{ij} are calculated using the hard-sphere equation
(B-6).
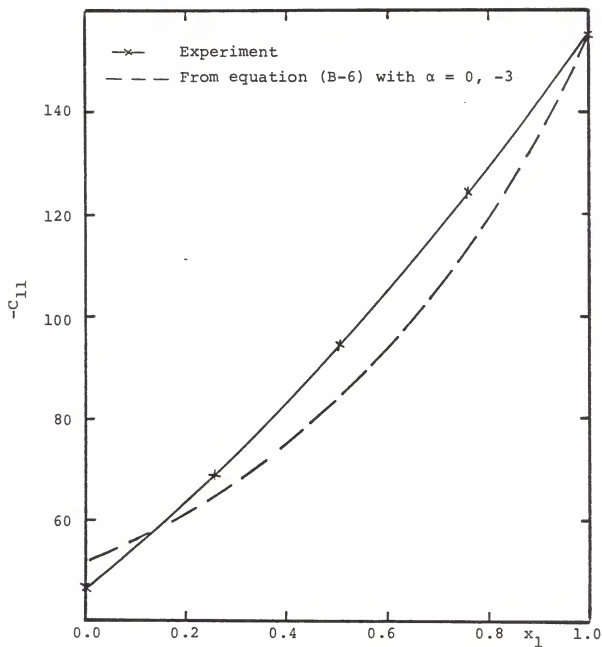
Figure 4-5. Isochoric (58.67 cc/mol) $-C_{11}$ values in acetone (l)-carbon disulphide at 273.15 K.

and γ relates the hard convex body volume (V), the hard convex body surface area (S), and the (1/4 Π)-multiple of the mean curvature of the hard convex body (R) by

$$\gamma = \frac{RS}{3V} \qquad (4-17)$$

This equation shows satisfactory agreement with computer simulations (Vieillard-Baron, 1974; Rebertus and Sando, 1977; Nezbeda and Boublik, 1978; Monson and Rigby, 1978) over the density range available. The Carnahan-Starling equation for hard sphere is recovered from equation (4-15) with $\gamma = 1$. The relation between the direct correlation function integral and the compressibility factor is given by the following expression

$$1 - C(\rho,T) = \frac{\partial P/RT}{\partial \rho}\bigg|_T = \frac{\partial \rho z}{\partial \rho}\bigg|_T \qquad (4-18)$$

Using equation (4-15) in equation (4-18), and

$$(1 - C) = \frac{1}{(1-\eta)^4} (1 + (6\gamma - 2)\eta$$
$$+ (9\gamma^2 - 6\gamma + 1)\eta^2 - 4\gamma\eta^3 + \gamma^2\eta^4) \qquad (4-19)$$

Values of (1-C) for different η and γ are presented in Table 4-5. The hard convex fluid shows less compressibility with larger γ. As complex molecules are non-spherical, the use of a hard sphere as the hard core

Table 4-5

(1-C) for Hard Convex Bodies

n	$Y = 1.$		$Y = 1.2$		$Y = 1.5$		$Y = 2.$	
.00	.1000	E01	.1000	E01	.1000	E01	.1000	E01
.10	.2189	E01	.2411	E01	.2764	E01	.3406	E01
.20	.4711	E01	.5534	E01	.6889	E01	.9469	E01
.30	.1025	E02	.1260	E02	.1657	E02	.2437	E02
.40	.2322	E02	.2955	E02	.4044	E02	.6233	E02
.50	.5700	E02	.7456	E02	.1052	E03	.1680	E03
.60	.1604	E03	.2147	E03	.3108	E03	.5102	E03
.70	.5714	E03	.7805	E03	.1155	E04	.1941	E04
.80	.3201	E04	.4454	E04	.6721	E04	.1153	E05
.90	.5580	E05	.7901	E05	.1214	E06	.2121	E06
.95	.9271	E06	.1324	E07	.2051	E07	.3616	E07

n	$Y = 3.$		$Y = 5.$		$Y = 8.$		$Y = 12.$	
.00	.1000	E01	.1000	E01	.1000	E01	.1000	E01
.10	.4855	E01	.8631	E01	.1622	E02	.3001	E02
.20	.1584	E02	.3340	E02	.7181	E02	.1456	E03
.30	.4440	E02	.1022	E03	.2333	E03	.4909	E03
.40	.1201	E03	.2917	E03	.6890	E03	.1480	E04
.50	.3370	E03	.8490	E03	.2052	E04	.4468	E04
.60	.1056	E04	.2734	E04	.6720	E04	.1478	E05
.70	.4120	E04	.1091	E05	.2716	E05	.6015	E05
.80	.2501	E05	.6742	E05	.1697	E06	.3782	E06
.90	.4690	E06	.1285	E07	.3262	E07	.7306	E07
.95	.8067	E07	.2226	E08	.5676	E08	.1274	E09

reference implies an adjustment in the hard sphere volume. The corrected volume is larger than the real volume because the compressibility for a convex body is smaller.

Table 4-6 presents the comparison of this adjustment. The corrected volume was chosen to minimize the difference between the (1-C) for a hard convex body and the (1-C) for a hard sphere. The adjustment is relatively good for $\eta \leq .5$ as shown in Figure 4-6. However, at higher values of the agreement is poorer.

Since the use of the hard convex body expression involves another parameter which probably cannot be chosen from molecular structure, given the relatively satisfactory agreement of the hard sphere equation and the expectancy that there must be further corrections to the model with perturbations, the hard sphere equation appears adequate at this stage.

4.5 Applications to Gases in Mixed Solvents

Mathias was very successful in using the model described in Section 4.2 in applications involving liquids containing supercritical components. This extends his analysis to calculate Henry constants in mixed solvents.

The common approach to calculate Henry's constants in mixed solvents involves Henry's constants in the pure solvents. The simplest relation was proposed by Kritchevski (1937) and is valid for an ideal behavior of the liquid phase

Table 4-6

Hard Convex Body-Hard Sphere Comparison

a) With $\gamma = 1.5$

n	$(1-C)^{hcb}$	$(1-C)^{hs}$	$(1-C)^{hs}_c$, $V^c=1.127V$	$(1-C)^{hcb}-(1-C)^{hs}_c$
.10	.2764 E01	.2189 01	.2413 E01	.3510 E00
.20	.6889 E01	.4712 E01	.5726 E01	.1163 E01
.30	.1654 E02	.1025 E02	.1390 E02	.2640 E01
.40	.4044 E02	.2322 E02	.3617 E02	.4270 E01
.50	.1052 E03	.5700 E02	.1077 E03	-.2500 E01
.60	.3108 E03	.1604 E03	.4099 E03	-.9910 E01
.70	.1155 E04	.5714 E03	.2552 E04	-.1397 E04
.80	.6721 E04	.3201 E04	.5959 E05	-.5287 E05

b) With $\gamma = 5.$

n	$(1-C)^{hcb}$	$(1-C)^{hs}$	$(1-C)^{hs}_c$, $V^c=1.420V$	$(1-C)^{hcb}-(1-C)^{hs}_c$
.10	.8631 E01	.2189 E01	.3022 E01	.5609 E01
.20	.3340 E02	.4712 E01	.9031 E01	.2437 E02
.30	.1022 E03	.1025 E02	.2905 E02	.7315 E02
.40	.2917 E03	.2322 E02	.1129 E03	.1785 E03
.50	.8490 E03	.5700 E02	.6615 E03	.1880 E03
.60	.2734 E04	.1604 E03	.1118 E05	-.8446 E04
.70	.1091 E05	.5714 E03	.4611 E10	-.4610 E10

$(1-C)^{hcb}$ is calculated from equation (4-19). $(1-C)^{hs}$ and the corrected $[(1-C)^{hs}_c]$ are calculated from equation (B-9).
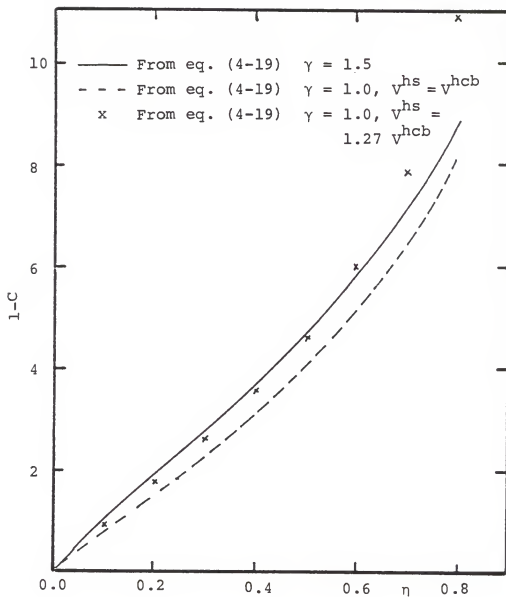
Figure 4-6. DCFI for pure component rigid
bodies.

$$\ln H_{1,m} = \sum_{i=2}^{n} x_i \ln H_{1,i} \tag{4-21}$$

where $H_{1,m}$ is the Henry constant of component 1 in a mixture m, and $H_{1,i}$ is the Henry constant in solvent i.

If the liquid phase behaves nonideally, equation (4-21) must be changed (O'Connell, 1971b; Prausnitz and Chueh, 1968)

$$\ln H_{1,m} - \sum_{i=2}^{n} x_i \ln H_{1,i}$$

$$= \lim_{x_1 \to 0} \gamma_{1,m} - \sum_{i=2}^{n} x_i \left(\lim_{x_1 \to 0} \gamma_{1,i} \right) \tag{4-22a}$$

or in unsymmetric convention

$$\ln H_{1,m} - \sum_{i=2}^{n} x_i \ln H_{1,i}$$

$$= \lim_{x_1 \to 1} \gamma_{1,m}^{*} - \sum_{i=2}^{n} x_i \left(\lim_{x_1 \to 1} \gamma_{1,i}^{*} \right) \tag{4-22b}$$

Depending on the model used to describe the activity co-efficient different forms of equation (4-22a) appear. Two of them are discussed in O'Connell's work. The first uses the Margules expression and transforms equation (4-22a) into

$$\ln H_{1,m} - \sum_{i=2}^{n} x_i \ln H_{1,i} = \sum_{i>k}^{n} \sum_{k=2}^{n-1} \alpha_{ik} \, x_i x_k$$

$$= - \frac{g^E}{RT} \quad \text{(solvents only)} \quad (4-23)$$

For a particular case of a solute in a binary solvent equation (4-23) reduces to

$$\ln H_{1,m} - x_2 \ln H_{1,2} - x_3 \ln H_{1,3} = -\alpha_{23} \, x_2 x_3$$

$$= - \frac{g^E}{RT} \quad \text{(solvents only)}$$

$$(4-24)$$

The second derives from a model of fluctuation solution theory presented in Chapter 2. In the case of binary solvents take the following form

$$\ln H_{1,m} - x_2 \ln H_{1,2} - x_3 \ln H_{1,3}$$

$$= \frac{x_3}{2} \left. \frac{\partial \ln \gamma_3}{\partial x_3} \right|_{T,P,N_2} + A_{23} \, \phi_2 \phi_3 \qquad (4-25)$$

where

$$A_{23} = \frac{1050 \, |v_2^o - v_3^o|}{T^{1/2} \, v_2^o \, v_3^o} \qquad (4-26)$$

ϕ_i is the volume fraction of solvent i in pure solvents

$$\phi_i = \frac{x_i v_i^o}{x_1 v_1^o + x_2 v_2^o} \qquad (4\text{-}27)$$

Other alternatives are to change the mole fraction in equation (4-22) to volume fraction, the surface fraction, or by using the r(volume) and q(surface) parameters of the UNIQUAC activity coefficient model (Abrams and Prausnitz, 1975).

The Mathias method uses the following equation

$$\ln H_{1,m} = \ln H_{1,R} + \ln \gamma_1 \ (T, \rho^f = \rho_m, \ \rho^r = \rho_R) \quad (4\text{-}28)$$

where

$$\frac{1}{\rho_m} = \sum_{i=2}^{3} x_i^{SF} v_i^o + v^E \ (T, \underline{x}^{SF}) \qquad (4\text{-}29)$$

with $\underline{x}^{SF}$ as the mole fractions free of solute.

Equation (4-28) comes from equation (A-4) for the variation of solute fugacity from infinite dilution in one solvent (R) to infinite dilution in another (mixture, m, here); γ_1 is calculated using equation (A-4). The binary constant k_{1i} is determined from k_{1R} and data on $H_{1,i}$ and $H_{1,R}$ to insure consistency in the limit $x_i \rightarrow 1$.

Table 4-7 presents results comparing Henry's constant calculations for 40 binary solvent systems. The numbers in the table indicate the absolute average difference

Table 4-7

Absolute Average Deviation in Calculated Henry's Constants for Gases in Binary Solvents

System	(4-21)	(4-24)	(4-25)	(4-21),V	(4-21),S	(4-21),r	(4-21),q	(4-28)	(4-28),$v^E=0$
1	44.2	7.77	9.72	+ 37.4	+ 39.6	+ 36.7	+ 32.7	11.03	+ 33.61
2	7.91	9.41	8.5	4.85	5.68	6.74	6.77	4.11	- 6.67
3	1.41	26.1	28.0	1.48	1.44	3.28	3.38	- 3.9	- 7.84
4	2.73	13.1	11.4	1.27	1.76	.63	.59	6.0	- 8.47
5	13.71	12.46	4.73	+ 4.86	+ 7.77	+ 5.44	+ 8.53	- 8.11	+ 8.93
6	15.56	12.90	6.67	+ 11.27	+ 12.65	+ 11.93	+ 14.08	+ 5.46	+ 12.89
7	78.54			+148.9	+123.2	+146.0	+138.22	+144.76	+161.72
8	23.98			+ 15.44	+ 18.17	+ 15.73	+ 16.53	+ 12.75	+ 21.63
9	11.5			+ 8.91	+ 9.76	+ 9.13	+ 8.16	+ 8.20	+ 9.66
10	9.10			+ 6.7	+ 7.5	+ 6.92	+ 6.03	+ 5.53	+ 7.29
11	12.6			+ 11.35	+ 11.62	+ 11.27	+ 11.	+ 2.71	+ 7.06
12	10.59			+ 9.89	+ 10.12	+ 9.83	+ 9.6	+ .70	+ 5.92
13	13.13	1.02	.46	+ 13.2	+ 13.17	+ 13.25	+ 13.23	+ 11.74	+ 11.74
14	4.53			- 1.0	- .79	- 1.02	- 2.60	- .95	- .93
15	.82	25.63	20.61	1.57	1.21	1.07	.85	.81	.83
16	8.05			- 4.74	.86	1.53	4.38	+ 4.91	- 5.61
17	7.85	10.72	4.64	.22	2.48	3.2	4.94	.573	+ 3.4
18	13.25	23.82	10.45	- 18.27	- 16.53	- 18.36	- 17.01	- 11.56	- 13.88
19	3.23	4.25	1.79	+ 6.12	+ 5.15	+ 6.39	+ 3.62	+ 5.12	+ 4.44
20	1.3	2.54	1.34	+ .72	- .89	.74	- 1.32	- 2.92	- .87

Table 4-7. Continued.

System	(4-21)	(4-24)	(4-25)	(4-21),V	(4-21),S	(4-21),r	(4-21),q	(4-38)	(4-28),$v^E=0$
21	2.15	11.8	2.6	-12.94	- 9.25	-12.77	-10.98	- 4.33	-11.20
22	11.13	21.99	5.90	-33.53	-26.67	-24.27	11.72	+ 2.89	-28.61
23	5.87	13.12	16.00	-29.38	-20.95	-17.77	5.97	+ 7.38	-24.68
24	11.10	6.23	30.84	-23.83	-13.62	-10.32	+ 9.94	+14.44	-19.31
25	13.85	23.2	8.38	-40.0	-30.68	-36.86	-26.91	2.21	-33.01
26	7.51	17.57	16.34	-38.38	-27.6	-34.54	-23.01	1.80	-31.81
27	4.84	11.07	26.16	-35.9	-23.57	-31.3	-18.10	2.2	-29.61
28	6.02	7.43	32.03	-34.2	-21.0	-29.16	15.16	2.97	-28.03
29	16.67	26.84	7.24	-36.29	-30.06	-28.03	17.24	3.13	-32.59
30	8.00	12.6	17.5	25.27	18.51	16.26	7.93	7.78	22.81
31	12.43	5.08	32.55	26.38	-16.07	11.92	11.44	9.31	-24.29
32	14.08	22.5	10.77	-37.01	-29.02	-34.49	25.53	5.12	30.31
33	20.03	6.01	39.23	-34.05	-20.80	-29.6	-13.86	5.97	26.01
34	36.71	14.98	57.14	27.14	15.49	22.43	9.27	+ 9.11	21.03
35	8.95	16.62	10.18	-32.35	-24.48	-21.39	9.21	5.91	-29.87
36	8.94	6.20	25.76	-25.16	16.37	12.42	8.23	11.35	23.73
37	19.96	11.09	45.51	28.09	15.97	23.9	10.09	+14.36	21.23
38	25.75	5.86	39.91	-28.84	-15.03	-23.64	7.87	4.5	-23.13
39	6.81	11.74	25.94	-37.71	-25.94	-21.18	6.13	+ 5.94	-35.01
40	33.26	11.02	60.62	-34.61	-17.34	-28.75	9.26	5.80	-26.71

Table 4-7. Continued.

Numbers in column 1 correspond to systems in Table 4-8.
The headings of columns 2 to 9 are the numbers of the equations in Section 4-5.
V stands for volume fraction, S stands for surface fraction, r stands for parameter r fraction, and q stands for parameter q fraction.
Numbers in the table are absolute average deviation. A positive sign indicates that mostly positive deviations occur. A negative sign indicates that mostly negative deviations occur. No sign indicates that deviations are negatives and positives.
In columns 2, 3, and 4 the sign of the deviations has not been considered.

between the calculated and the experimental values. Table 4-8 contains the reference of the data and the systems involved.

The numbers obtained with the Mathias model are excellent considering that experimental variations in gas solubility are large. (Errors of 10.0% are expected.) Except for the extremely large error in the acetylene-acetone-n-hexane system, the agreement is generally good provided the excess volume is included. Otherwise, the results are comparable to all other methods which are roughly the same. Table 4-9 presents average deviations for all but that system. To indicate the difficulty of describing the alcohol-water mixtures (22-40) we have separated these out. It is clear that Mathias model produces a better prediction for the Henry constant, particularly in aqueous alcohols.

Table 4-8

Binary Solvent Systems

System	Gas	Solvents	T, K	N° of data	Reference
1	CO	Carbon disulphide-Acetone	298.15	4	Smith (1928)
2	CO	Toluene-Aniline	298.15	5	Smith (1928)
3	CO	Benzene-Aniline	298.15	5	Smith (1928)
4	CO	Benzene-Nitrobenzene	298.15	3	Smith (1928)
5	CO	Toluene-Acetic acid	298.15	3	Smith (1928)
6	CO	Benzene-Acetic Acid	298.15	3	Smith (1928)
7	C_2H_2	Acetone-Hexane	248.1	3	Leites and Ivanovsky (1962)
8	C_2H_4	Acetone-Hexane	243.1	3	Leites and Ivanovsky (1962)
9	C_2H_4	Toluene-Heptane	213.15	3	Leites and Ivanovsky (1962)
10	C_2H_4	Toluene-Heptane	223.15	3	Leites and Ivanovsky (1962)
11	C_2H_4	Toluene-Methylcyclohexane	213.15	3	Leites and Ivanovsky (1962)
12	C_2H_4	Toluene-Methylcyclohexane	223.15	3	Leites and Ivanovsky (1962)

Table 4-8. Continued.

System	Gas	Solvents	T, K	N° of data	Reference
13	H_2	Acetone-Isopropanol	298.15	5	Puri and Ruether (1974)
14	N_2	Cyclohexane-Isooctane	298.15	9	Nitta et al. (1973)
15	N_2	Ethanol-Benzene	298.15	9	Nitta et al. (1978)
16	N_2	Ethanol-Diethyl ether	273.15	9	Nitta et al. (1978)
17	N_2	Ethanol-Ethyl acetate	313.15	9	Nitta et al. (1978)
18	CO_2	Chloroform-Methanol	293.15	4	Koudelka (1964)
19	CO_2	Acetone-Benzene	293.15	5	Koudelka (1964)
20	CO_2	Chloroform-Benzene	293.15	4	Koudelka (1964)
21	CO_2	Acetone-Methanol	293.15	4	Koudelka (1964)
22	Ar	Methanol-Water	278.15	7	Ben-Naim (1967)
23	Ar	Methanol-Water	288.15	7	Ben-Naim (1967)
24	Ar	Methanol-Water	298.15	7	Ben-Naim (1967)
25	Ar	Ethanol-Water	278.15	9	Ben-Naim and Baer (1964)
26	Ar	Ethanol-Water	288.15	9	Ben-Naim and Baer (1964)

Table 4-8. Continued.

System	Gas	Solvents	T, K	N° of data	Reference
27	Ar	Ethanol-Water	298.15	9	Ben-Naim and Baer (1964)
28	Ar	Ethanol-Water	303.15	9	Ben-Naim and Baer (1964)
29	O_2	Methanol-Water	273.15	10	Tokunaga (1974)
30	O_2	Methanol-Water	293.15	14	Tokunaga (1974)
31	O_2	Methanol-Water	313.15	10	Tokunaga (1974)
32	O_2	Ethanol-Water	273.15	15	Tokunaga (1974)
33	O_2	Ethanol-Water	293.15	10	Tokunaga (1974)
34	O_2	Ethanol-Water	313.15	12	Tokunaga (1974)
35	N_2	Methanol-Water	392.15	13	Tokunaga (1974)
36	N_2	Methanol-Water	313.15	12	Tokunaga (1974)
37	N_2	Ethanol-Water	293.15	13	Tokunaga (1974)
38	N_2	Ethanol-Water	313.15	14	Tokunaga (1974)
39	CH_4	Methanol-Water	293.15	7	Tokunaga and Kawai (1974)
40	CH_4	Methanol-Water	293.15	7	Tokunaga and Kawai (1974)

Table 4-9

Average of the Absolute Average Deviations of Table 4-8

System	(4-21)	(4-24)	(4-25)	(4-21),v	(4-21),S	(4-21),r	(4-21),q	(4-28)	(4-28),$v^E=0$
1-21	10.38	12.42	8.53	8.51	8.82	8.80	8.80	5.57	9.14
22-40	14.31	13.21	26.70	32.53	21.53	25.60	13.00	6.43	26.93
1-40	12.30	12.80	19.30	20.00	15.01	16.97	10.85	5.99	18.04

Numbers in column one correspond to systems in Tables 4-7 and 4-8.
The headings V, S, r, q have the same meaning as that in Table 4-7.

CHAPTER 5

AN APPLICATION TO LIQUID-LIQUID EQUILIBRIA

5.1   Introduction

As pointed out in Chapter 4, the fluctuation solution
theory is successful in describing the gas-liquid equi-
libria. A more severe test to the model is its application
to liquid-liquid equilibria. For the latter, no model
covers all aspects of two or more fluid phases in equi-
librium. This chapter describes application of the model
of Chapter 4 to this problem.

In a binary system, there are two pure component
choices for the lower limit in the integral equations of
the fluctuation solution theory. For each reference, the
model contains one binary parameter. Due to the imperfec-
tions in the model, the calculated results and parameters
are different for the different references. The agreement
with data, while good, is not perfect. In order to improve
the situation we try different ways to use the equations
with two references. One of them, the multifluid approach,
combines the calculation of different references. The ex-
tension to multicomponent systems is straightforward.

Section 5.2 presents results using one parameter for
each binary pair. Section 5.3 describes the use of two

parameters for each binary. In section 5.4, we present
the multifluid approach and its results.

5.2 Calculations of Liquid-Liquid Equilibria Using One Reference

Two different classes of models have been used in
correlating liquid-liquid equilibria:

a) Models which empirically describe the distribution
ratios. Laddle and Degalasen (1978) present a good summary
of these methods. All of them suffer from the disadvantage
of working for only ternary systems and of requiring ex-
perimental ternary tie lines as input information.

b) Models which have some semitheoretical basis.
Sørensen et al. (1977) present an excellent review with
extensive comparisons between methods. In general, these
models describe the excess Gibbs free energy as a function
of composition and temperature. The UNIQUAC (Abrams and
Prausnitz, 1975) equation is the most convenient for cor-
relating data, but it is not completely successful.

Most binary liquid mixtures have an upper critical
solution temperature due to the balance of the entropy
of mixing against the interaction energy of the molecules.
More complex mixtures, such as amines in solution with
water, generate temperature-composition phase diagrams
with an upper and a lower critical solution temperature.
This behavior can be understood by the presence of highly
directional interactions, such as hydrogen bonds. The

models mentioned above do not provide a good correlation of these closed-loop diagrams. For these cases, the most successful theories are applications of the Ising model (gas-lattice models (Wheeler and Andersen, 1980; Goldstein and Walker, 1983)).

In order to predict binary and multicomponent liquid-liquid equilibria, it is necessary to have a method for predicting activity coefficients. The UNIFAC (Fredenslund et al., 1975) method, a group contribution model, is one of such methods. Magnussen et al. (1981) built a group interaction parameter table suited for liquid-liquid equilibria. Their results indicate that only a semi-quantitative prediction is possible.

We shall use the model for the direct correlation function integrals described in section 3.2, together with equations given in section 2.4, to correlate liquid-liquid equilibria in binary and multicomponent mixtures.

The procedure to do the calculations involves an iterative calculation with the following six steps:

1) Fitting of pure component characteristic parameters. We evaluate T^* and V^* with equation (4-4) and P-V-T data. Table 5-1 presents the characteristic parameters for substances involved in our liquid-liquid equilibrium calculations.

2) Calculation of final solution density. A numerical solution is found for equation (4-12). To do this, we need guesses of the binary parameter and mixture composition.

Table 5-1

Characteristic Parameters for Compounds Involved in Liquid-Liquid Equilibria

Compound	T*, K	T_c, K	V*, cm^3/gmol	V_c, cm^3/gmol
Methane	195.1	190.6	100.1	99.0
n-Hexane	492.9	507.4	372.9	370.0
n-Heptane	578.1	537.2	433.0	440.0
Carbon disulphide	413.7	552.0	167.8	170.0
Tetrafluormethane	220.0	227.6	153.2	140.0
Acetone	405.2	508.1	200.6	209.0
n-Butanol	450.3	562.9	268.2	43.6
Cyclohexane	616.1	553.4	317.1	308.0
Aniline	604.1	699.0	289.4	324.0
Water	459.2	647.3	46.5	56.0

All critical constants listed are from Reid et al. (1976).

3) Calculation of activity coefficients. Activity coefficients are found from equation (A-4) using the binary parameter, composition, and calculated solution density of step 2.

4) Confirmation of equilibrium composition. Steps 2 and 3 are done for each phase present in the equilibrium. The isoactivity condition expressed by equation (2-50) is now checked. If the calculated activity coefficients do not satisfy equation (2-50), a new composition of the solution in each phase is guessed, and steps 2 and 4 are repeated.

5) Confirmation of stability. If the two phases follow the isoactivity requirement, we check material stability. If the phases do not satisfy this condition, a new composition is guessed, and steps 2 and 5 are repeated.

6) Comparison of experimental and calculated concentrations. If the error is larger than expected, the binary parameters are changed, and steps 2 to 6 are repeated until further changes do not improve the agreement.

Winnick and Powers (1966a,b) made a detailed study of the acetone-carbon disulphide system. At 0°C and atmospheric pressure this system is completely miscible, but at pressures over 5000 atmospheres partial miscibility can be observed. They measured the mixing volume as a function of pressure and temperature, and the phase behavior at high pressure. They used the volumetric data

to calculate equilibrium composition. Figure 5-1 shows the observed phase behavior that calculated with the volumetric data and that calculated using the fluctuation solution theory. Agreement between calculated and experimental is better using direct correlation function integrals than using volumetric data. Attempts to improve the agreement by changing the values of the characteristic parameters (T* and V*) were unsuccessful and Figure 5-1 gives the best representation of the method. However, the uncertainties in this system are large since even the calculated phase behavior of Winnick and Powers does not agree with experiment.

An alternative system is that of Keyes and Hildebrand (1917) who studied the aniline-hexane system. They measured solubility, mixing volume, heat of mixing, surface tension, and compressibility in the mixture. Figure 5-2 displays the experimental points and the calculated phase envelope from the present method. The agreement is quite good. To observe the effect of the characteristic parameters T* and V* on the phase envelope, we changed their values and made calculations using the six step procedure. These changes do not affect the shape of the phase envelope. Rather they move its position in a temperature-composition diagram. Figure 5-3 presents a schematic picture of these displacements using the upper critical solution temperature (CST). These changes do not produce an improved correlation of
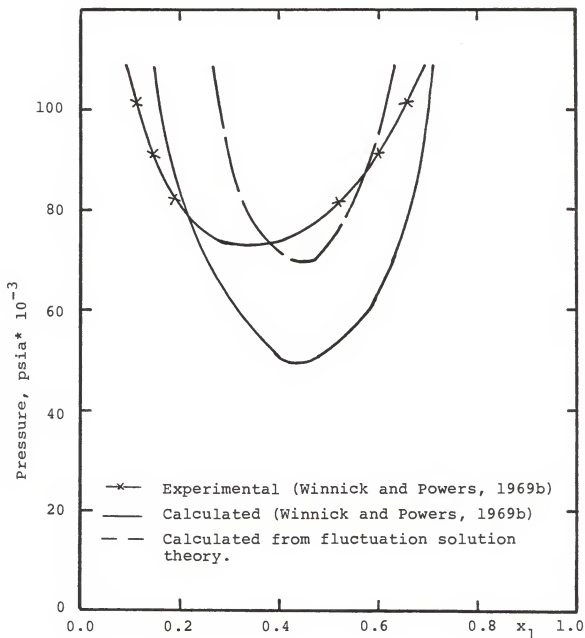
Figure 5-1. Pressure dependence of liquid-liquid
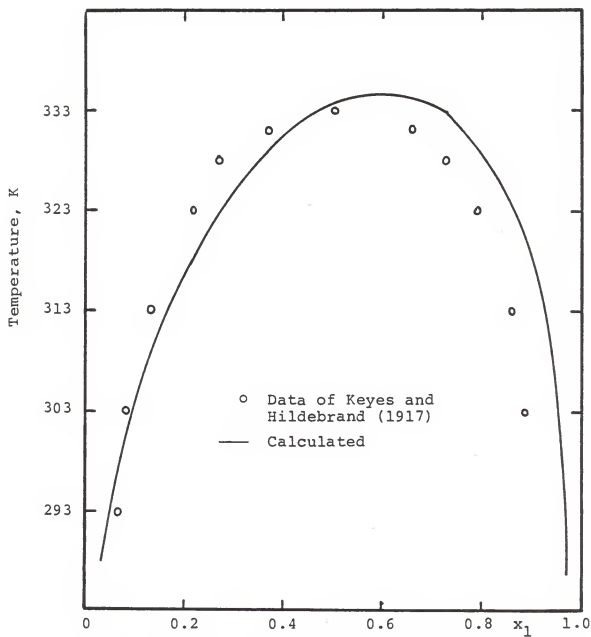equilibria for acetone (1)-carbon
disulphide (2) at T = 273.15 K.

Figure 5-2. Temperature dependence of liquid-liquid equilibria for aniline (1)-hexane (2) at 1 atm.
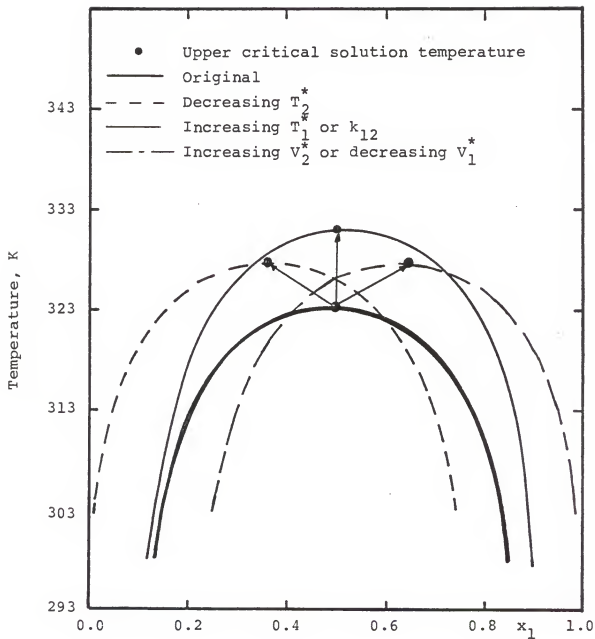
Figure 5-3. Movement of upper critical solution
temperature and liquid-liquid phase
envelope of aniline (1)-n-hexane (2)
system with changes in parameters.

the liquid-liquid equilibria for aniline-hexane. The phase
envelope in Figure 5-2 is our best calculation.

In order to compare the results from the fluctuation
solution theory with those of UNIQUAC, an analysis of the
aniline-cyclohexane is made. Angelescu and Guisca (1942)
measured the solubility in aniline-cyclohexane mixtures.
Their results are presented in Table 5-2. Eckert et al.
(1980) examined this system with the UNIQUAC model. Table
5-2 presents their findings. They analyzed an extension
of UNIQUAC using four parameters by allowing the original
parameters to be linear functions of temperature. Though
this provides a better correlation than the original two-
parameter model, we have chosen to do the comparison with
the original UNIQUAC. Table 5-2 presents the composition
calculated with the fluctuation solution theory using pure
aniline as the reference state. Figure 5-4 displays
comparisons between experimental and calculated composi-
tions. For this particular system, the correlation given
by the fluctuation solution theory is better than the one
given by the original UNIQUAC model.

5.3 Calculations of Liquid-Liquid Equilibria
         Using Two References

The main problem with the model described in section
5.2 is that it contains only one parameter whose value
depends on the reference state. Thus the compositions in
the two phases in a binary system cannot be matched. An-
other way to look at the problem of the model is by doing

Table 5-2

Comparison of Models in Correlating Liquid-Liquid Equilibria for
Aniline (1)-Cyclohexane (2)

T, K	x_1, phase '			x_1, phase "		
	Exp.	FST	UNIQUAC	Exp.	FST	UNIQUAC
280.15	.060	.068	.180	.832	.952	.69
280.15	.0720	.088	.200	.823	.936	.685
287.15	.093	.120	.230	.814	.900	.673
290.15	.110	.160	.250	.796	.872	.650
294.15	.130	.212	.278	.755	.832	.630
297.15	.163	.280	.288	.738	.772	.620
301.15	.228	.392	.300	.670	.660	.600

The experimental data (Exp.) are from Angelescu and Giusca (1942).
The fluctuation solution theory data (FST) were calculated using aniline as
reference and $k_{12} = 0.2514$.
The UNIQUAC data are from Eckert et al. (1980).
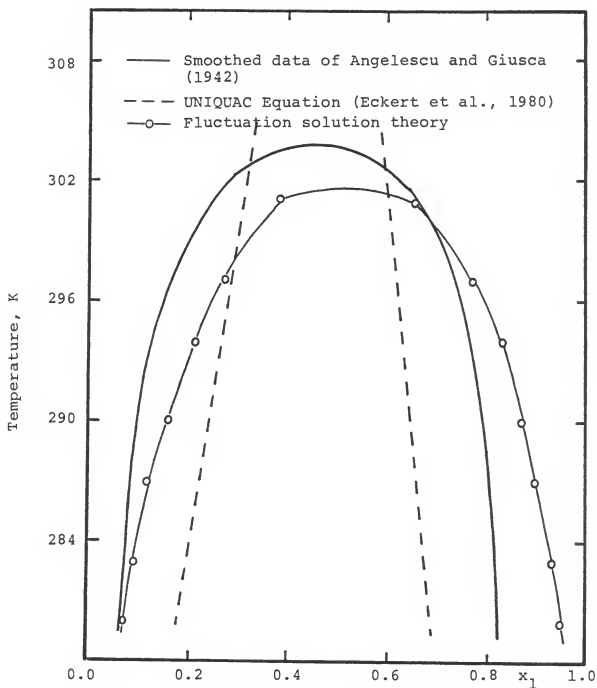
Figure 5-4. Temperature dependence of liquid-liquid equilibria for aniline (1)-cyclohexane (2) at P = 1 atm.

density calculations using different references. Figure 5-5 displays the differences that exist when a different reference is chosen to do the calculation of the solution density. The density of one pure component cannot be predicted accurately using only the reference density and equation (4-12).

Experience shows that in predicting ternary systems, the best starting point is a perfect match for the immiscible pairs. Other models have overcome this difficulty by having two binary parameters. Thus, we shall try two alternatives to introduce a second binary parameter in our model and provide similar matching:

a) Use one binary parameter for each phase with a single reference for both phases.

b) Use of different references for each phase, each having its own binary parameter. For the case of Figure 5-5 this alternative implies using hexane as reference in the hexane-rich side and aniline in the aniline-rich side.

Table 5-3 presents the calculations for the system aniline-cyclohexane at 10°C using alternatives a and b.

Two observations can be made:

1) One reference, two parameters (alternative a) is only as good as one reference one parameter.

2) Two references, two parameters (alternative b) is equivalent to one reference, one parameter in each phase. Most importantly, calculations of the binodal curve yielded poor or no convergence.
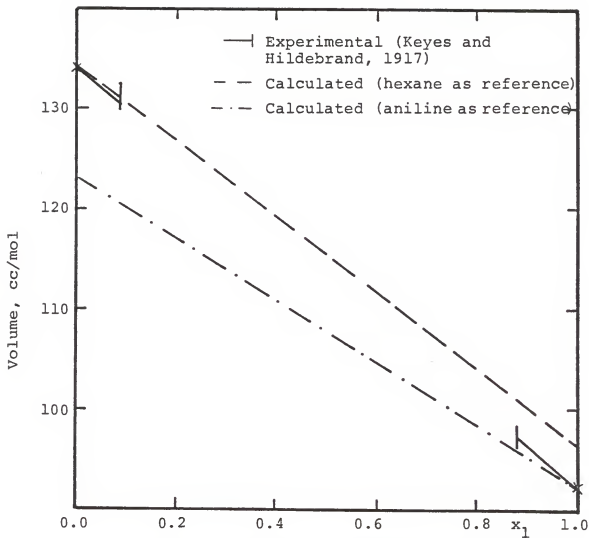
Figure 5-5. Solution volumes for aniline (1)-
hexane (2) at T = 298.15 K.

Table 5-3

Comparison of Tie Line Calculations Using Different
Binary Parameters and Different References for
Aniline (1)-Cyclohexane (2) at 10°C

1. Reference: Cyclohexane

   a. Binary parameter = .026
      x_1, phase' = .1118 x_1, phase" = .9121

   b. Binary parameter = .03
      x_1, phase ' = .0666 x_2, phase" = .9493

   c. Binary parameter cyclohexane side = .026,
      binary parameter aniline side = .03
      x_1, phase' = .0621 x_2, phase" = .9491

   d. Binary parameter cyclohexane side = .03,
      binary parameter aniline side = .26
      x_1, phase' = .1402 x_2, phase" = .9133

2. Reference: Aniline

   a. Binary parameter = .026
      x_1, phase' = .0786 x_1, phase" = .9401

   b. Binary parameter = .03
      x_1, phase' = .0464 x_1, phase" = .9657

   c. Binary parameter cyclohexane side = .026,
      binary parameter aniline side = .03
      x_1, phase' = .0783 x_1, phase" = .9333

   d. Binary parameter cyclohexane side = .03,
      binary parameter aniline side = .026
      x_1, phase' = .0464 x_1, phase" = .9672

3. Reference: Aniline and cyclohexane

   a. Binary parameter cyclohexane side = .026,
      binary parameter aniline side = .03
      x_1, phase' = .1215 x_1, phase" = .9679

   b. Binary parameter cyclohexane side = .03,
      binary parameter aniline side = .026
      x_1, phase' = .0659 x_1, phase" = .9392

4. Experimental (Angelescu and Giusca, 1942).

      x_1, phase' = .072 x_1, phase" = .823

In order to clarify the results obtained in the calculations using two binary parameters and two references, we look at the shape of the chemical potential against composition. The system tetrafluormethane-methane is appropriate because it shows partial miscibility between 87 K and 95 K at atmospheric pressures, and there is extensive information about the system (Croll and Scott, 1958; Thorp and Scott, 1956; Simon and Knobler, 1971; Paas and Schneider, 1979). The results of the chemical potential for the tetrafluormethane-methane mixtures are presented in Tables 5-4, 5-5, and 5-6. In Tables 5-4 and 5-6 we can see that an increase in the binary parameter produces an increase in the chemical potential. The increase is larger at infinite dilution for both components; near pure composition, the variation is small. Table 5-5 shows the obvious result that the chemical potentials are equal when the references and the binary parameters are equal. While the chemical potential curve for a particular component is completely different when calculated with two references and two parameters near pure component, it is practically the same as when calculated with one reference and two parameters.

Now, it is possible to explain the behavior of the calculations in the aniline-cyclohexane system. We made the observation that the alternative a (use of one reference and two paramters) is equivalent to one reference, one parameter. The equilibrium is found by matching two

Table 5-4

Chemical Potentials and Densities for $CF_4(1)$-$CF_4(2)$ Mixtures

with $^1k_{12} = .03$, $^2l_{12} = .03$

x_1	$-^1\mu_1 \times 10^{-2}$	$-^2\mu_1 \times 10^{-2}$	$-^1\mu_2 \times 10^{-2}$	$-^2\mu_2 \times 10^{-2}$	^1v	^2v
0.00	∞	∞	.2029	.2900	30.90	35.34
0.10	.2885	.4257	.2026	.2899	32.71	37.56
0.20	.3017	.4367	.2003	.2880	34.45	39.49
0.30	.3129	.4456	.1966	.2849	36.12	41.19
0.40	.3216	.4530	.1919	.2809	37.75	42.72
0.50	.3280	.4586	.1867	.2763	39.34	44.14
0.60	.3324	.4626	.1813	.2715	40.90	45.50
0.70	.3352	.4652	.1762	.2667	42.44	46.83
0.80	.3367	.4665	.1720	.2628	43.96	48.15
0.90	.3370	.4668	.1704	.2615	45.46	49.46
1.00	.3364	.4662	∞	∞	46.96	50.79

The chemical potential is in cal/g mole. The volume is in cm^3/g mole.
The superscript indicates the reference used, e.g., $^1\mu_1$ is the chemical potential of component 1 calculated using component 1 as reference.
In the case of the binary parameters, the superscript indicates the side in which the parameter is used, e.g., $^1k_{12}$ is the binary parameter used in side 1 or in the side that is rich in tetrafluormethane.

Table 5-5

Chemical Potentials and Densities for $CF_4(1)-CH_4(2)$ Mixtures with
$^1k_{12} = .03$, $^2k_{12} = .03$

x_1	$-^1\mu_1 \times 10^{-2}$	$-^1\mu_1 \times 10^{-2}$	$-^1\mu_2 \times 10^{-2}$	$-^1\mu_2 \times 10^{-2}$	^1v	^1v
0.00	∞	∞	.2029	.2029	30.90	30.90
0.10	.2885	.2885	.2026	.2026	32.71	32.71
0.20	.3017	.3017	.2003	.2003	34.45	34.45
0.30	.3129	.3129	.1966	.1966	36.12	36.12
0.40	.3216	.3216	.1919	.1919	37.75	37.75
0.50	.3280	.3280	.1867	.1867	39.34	39.34
0.60	.3324	.3324	.1812	.1813	40.90	40.90
0.70	.3352	.3352	.1762	.1762	42.44	42.44
0.80	.3367	.3367	.1720	.1720	43.96	43.96
0.90	.3370	.3370	.1704	.1704	45.46	45.46
1.00	.3364	.3364	∞	∞	46.96	46.96

The chemical potential is in cal/g mole. The volume is in cm^3/g mole.
The superscript indicates the reference used, e.g., $^1\mu_1$ is the chemical potential of component 1 calculated using compoient 1 as reference.
In the case of the binary parameters, the superscript indicates the side in which the parameter is used, e.g., $^1k_{12}$ is the binary parameter used in side 1 or in the side that is rich in tetrafluormethane.

Table 5-6

Chemical Potentials and Densities for $CF_4(1)$-$CH_4(2)$ Mixtures with

$^1k_{12} = .03$, $^2k_{12} = .10$

x_1	$-^1\mu_1 \times 10^{-2}$	$-^2\mu_1 \times 10^{-2}$	$-^1\mu_2 \times 10^{-2}$	$-^2\mu_2 \times 10^{-2}$	^1v	^2v
0.00	∞	∞	.2029	.2900	30.90	35.34
0.10	.2885	.3314	.2026	.2877	32.71	39.43
0.20	.3017	.3697	.2003	.2811	34.45	43.54
0.30	.3129	.3971	.1966	.2720	36.12	46.61
0.40	.3216	.4182	.1919	.2607	37.75	47.52
0.50	.3280	.4351	.1867	.2468	39.34	47.83
0.60	.3324	.4481	.1813	.2310	40.90	48.19
0.70	.3352	.4574	.1762	.2139	42.44	48.66
0.80	.3367	.4632	.1720	.1965	43.96	49.26
0.90	.3370	.4660	.1704	.1810	45.46	49.98
1.00	.3364	.4662	∞	∞	46.96	50.79

The chemical potential is in cal/g mole. The volume is in cm^3/g mole. The superscript indicates the reference used, e.g., 1 is the chemical potential of component 1 calculated using component 1 as reference. In the case of the binary parameters, the superscript indicates the side in which the parameter is used, e.g., $^1k_{12}$ is the binary parameter used in side 1 or the side that is rich in tetrafluormethane.

chemical potential curves. In these cases, the curves
are identical at high concentrations of the component.
As a consequence, they cannot be distinguished. The be-
havior of alternative b is due to the same effect; each
phase follows the behavior of the curves near pure com-
ponent for chemical potential matching.

5.4 Calculations of Liquid-Liquid Equilibria Using a Multifluid Approach

To overcome the limitation of using one parameter, we
explore a multifluid approach that gives for a binary
system

$$\ln \gamma_i = x_1 \ln {}^1\gamma_i + x_2 \ln {}^2\gamma_i \qquad (5-1)$$

where the supraindex on the left indicates the substance
chosen as reference to do the calculations (e.g., ${}^1\gamma_i$ is
the activity coefficient of component i calculated using
component 1 as reference). By definition of $\ln \gamma_i$ we can
write

$$G^E = RT \sum_{i=1}^{n} x_i \ln \gamma_i \qquad (5-2)$$

then, combining equations (5-1) and (5-2)

$$G^E = x_1 {}^1G^E + x_2 {}^2G^E \qquad (5-3)$$

Excess enthalpy and excess volume are related with excess Gibbs energy through

$$\frac{\partial G^E}{\partial \rho}\Bigg|_{T,\underline{x}} = V^E \qquad (5-4)$$

$$\frac{\partial G^E/T}{\partial T}\Bigg|_{P,\underline{x}} = -\frac{H^E}{T} \qquad (5-5)$$

Now, using equation (5-3) in equations (5-4) and (5-5)

$$V^E = x_1 \, {}^1V^E + x_2 \, {}^2V^E \qquad (5-6)$$

and

$$H^E = x_1 \, {}^1H^E + x_2 \, {}^2H^E \qquad (5-7)$$

Table 5-7 shows the results of the tetrafluormethane-methane system in the partially and completely miscible regions. The binary parameters ${}^1k_{12}$ and ${}^2k_{12}$ were obtained from liquid-liquid equilibria at 89 K and estimated from the excess Gibbs free energy at 110 K. A linear function of temperature was used for all the other data. The agreement between calculated excess Gibbs energy and excess volume with experimental data is quite good.

The aniline-cyclohexane system in the partially and completely miscible regions is examined thoroughly here. The calculations cover liquid-liquid equilibrium composition excess Gibbs free energy, excess volume, and excess enthalpy. In Table 5-8 the binary parameters ${}^1k_{12}$ and ${}^2k_{12}$ were

Table 5-7

Analysis of $CF_4(1)$-$CH_4(2)$ System

Liquid-Liquid Equilibria

T, K	x_1, phase' Exp.[a]	x_1, phase' Calc.[b]	x_1, phase" Exp.[a]	x_1, phase" Calc.[b]
89	.800	.800	.123	.123
90	.785	.775	.138	.131
91	.769	.749	.161	.142
92	.738	.720	.185	.156
93	.692	.689	.215	.173
94	.610	.655	.285	.195

Miscible Liquid Properties

x_1	G^E/RT (T = 110.5 K) Exp.[a]	G^E/RT (T = 110.5 K) Calc.[c]	V^E, cm³/g mole (T = 106.7 K) Exp.[a]	V^E, cm³/g mole (T = 106.7 K) Calc.[d]
0.10	.166	.161	.38	.32
0.25	.326	.315	.75	.57
0.50	.390	.383	.88	.55
0.75	.259	.265	.58	.29
0.90	.114	.121	.26	.11

[a] Experimental data from Croll and Scott (1958).
[b] Calculated using scheme of section 5.2 with equation (5-1).
[c] Calculated using equation (5-3).
[d] Calculated using equation (5-6).

Table 5-8

Analysis of Aniline (1)-Cyclohexane (2) System

Liquid-Liquid Equilibria

T, K	x_1, phase' Exp.[a]	x_1, phase' Calc.[c]	x_1, phase" Exp.[a]	x_1, phase" Calc.[c]
278.16	.827	.835	.056	.054
283.16	.823	.817	.072	.074
288.16	.810	.800	.094	.099
293.16	.775	.768	.122	.129
298.16	.72	.735	.173	.167
303.16	.592	.692	.31	.213

Miscible Liquid Properties

x_1	G^E/RT (T = 392.46 K) Exp.[b]	G^E/RT (T = 392.46 K) Calc.[d]	V^E_{calc}, cm^3/g mole (T = 392.46 K)
.10	.133	.126	.92
.25	.237	.278	1.80
.50	.384	.411	2.05
.75	.290	.340	1.21
.90	.146	.173	.42

[a] Experimental data from Angelescu and Giusca (1942)
[b] Experimental data from Há la et al. (1968).
[c] Calculated using scheme of Section 5.2 with equation (5-1).
[d] Calculated using equation (5-3).
Equation (5-6) was used to calculate the excess volume.

obtained from liquid-liquid equilibria at 278.15 K, 288.15 K, and 298.15 K. A linear interpolation was used for all the other calculations. In Table 5-9 the linear interpolation for the binary constants was done with the liquid-liquid equilibria at 278.16 K and 298.16 K. Figure 5-6 displays the results of Table 5-9. In Table 5-10 the binary parameter function of temperature was interpolated between the 278.15 K and 392.46 K data. Table 5-11 presents the results of calculations with UNIQUAC model using parameters given in the literature (Nicolaides and Eckert, 1978a). Finally, Table 5-12 compares experimental and calculated results using the UNIQUAC model and the fluctuation solution theory.

From all these results we can infer the following conclusions for fluctuation solution theory:

a) In the correlation mode with a linear dependence in the binary parameters, the description of the liquid-liquid equilibria is reasonably good (Table 5-8) with good results also obtained in the completely miscible region. Results of the same quality are obtained with only two sets of liquid-liquid equilibrium data (Table 5-9) or with one set of data in the partially miscible region and another in the miscible region (Table 5-10). The results calculated from the fluctuation solution theory are better than the results calculated using UNIQUAC (Table 5-11) which has large errors in the miscible region.

Table 5-9

Analysis of Aniline (1)-Cyclohexane (2) System

Liquid-Liquid Equilibria

T, K	x_1, phase'		x_1, phase"	
	Exp.[a]	Calc.[c]	Exp.[a]	Calc.[c]
278.16	.827	.827	.056	.056
283.16	.823	.809	.072	.077
288.16	.810	.786	.094	.102
293.16	.755	.757	.122	.134
298.16	.72	.720	.173	.173
303.16	.592	.662	.31	.222

Miscible Liquid Properties

x_1	G_E/RT (T = 392.46 K)		V_{calc}^E, cm^3/g mole (T = 392.46 K)
	Exp.[b]	Calc.[d]	
.10	.133	.125	.91
.25	.237	.276	1.78
.50	.384	.405	2.02
.75	.290	.335	1.19
.90	.146	.170	.48

[a]Experimental data from Angelescu and Giusca (1942).
[b]Experimental data from Hála et al. (1968).
[c]Calculated using scheme of Section 5.2 with equation (5-1).
[d]Calculated using equation (5-3).
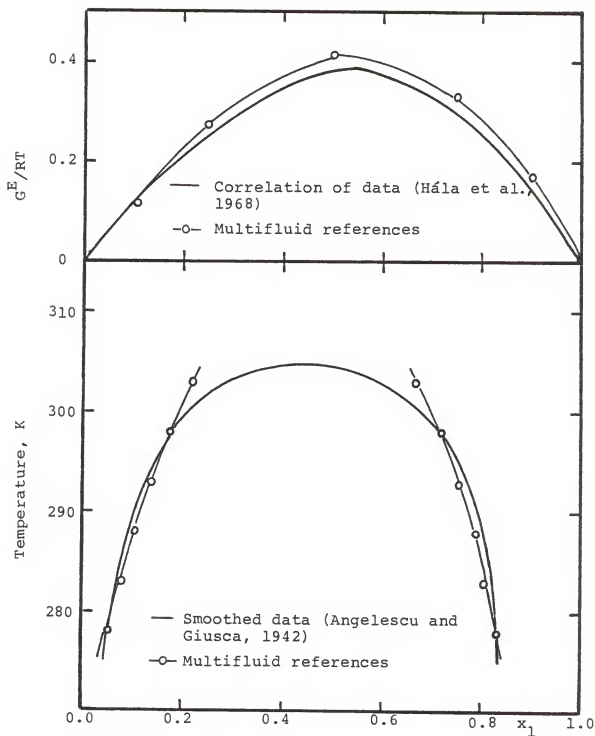Equation (5-6) was used to calculate the excess volume.

Figure 5-6. Correlation of liquid-liquid equilibria and excess Gibbs energy for aniline (1) and cyclohexane (2) using multifluid references.

Table 5-10

Analysis of Aniline (1)-Cyclohexane (2) System

Liquid-Liquid Equilibria

	x_1, phase'		x_1, phase"	
T, K	Exp.[a]	Calc.[c]	Exp.[a]	Calc.[c]
278.16	.827	.827	.056	.056
283.16	.823	.802	.072	.076
288.16	.810	.770	.094	.101
293.16	.775	.722	.122	.132
298.16	.72	.632	.173	.174
303.16	.592	.595	.31	.230

Miscible Liquid Properties

	G^E/RT (T = 392.46 K)		V^E_{calc}, cm^3/g mole (T = 392.46 K)
x_1	Exp.[b]	Calc.[d]	
.10	.133	.125	.93
.25	.237	.273	1.80
.50	.384	.394	2.00
.75	.290	.320	1.17
.90	.146	.160	.46

[a] Experimental data from Angelescu and Giusca (1942).
[b] Experimental data from Hála et al. (1968).
[c] Calculated using scheme of Section 5.2 with equation (5-1).
[d] Calculated using equation (5-3).
Equation (5-6) was used to calculate the excess volume.

Table 5-11

Analysis of Aniline (1)-Cyclohexane (2) System

Liquid-Liquid Equilibria

T, K	x_1, phase' Exp.[a]	Calc.[c]	x_1, phase" Exp.[a]	Calc.[c]
278.16	.827	.870	.056	.035
283.16	.823	.845	.072	.052
288.16	.810	.814	.094	.080
293.16	.775	.767	.122	.124
298.16	.720	.685	.173	.204
308.16	.592	.490	.310	.490

Miscible Liquid Properties

G^E/RT (T = 392.46 K)

x_1	Exp.[b]	Calc.[d]	Calc.[c]
.10	.133	.159	-.153
.25	.237	.324	-.343
.50	.384	.419	-.521
.75	.290	.306	-.457
.90	.146	.145	-.245

[a] Experimental data from Angelescu and Giusca (1942).

[b] Experimental data from Hála et al. (1968).

[c] Calculated using UNIQUAC, liquid-liquid parameters from Nicolaides and Eckert (1978a).

[d] Calculated using UNIQUAC, vapor-liquid parameters from Nicolaides and Eckert (1978b).

Table 5-12

Comparison of Excess Enthalpy Calculations in Aniline (1) -Cyclohexane (2)

h^E/R (T = 323.15 K)

x_2	Exp.	Calc.[a]	Calc.[b]
.0477	50.87	28.70	190.00
.1675	146.68	105.95	610.00
.3599	227.04	220.27	1030.00
.4505	242.65	259.08	1100.00
.6456	240.40	283.43	1010.00
.8718	155.14	163.13	520.00

h^E/R (T = 298.15 K)

x_2	Exp.	Calc.[a]	Calc.[b]
.0483	51.38	37.28	144.00
.1751	148.61	143.71	478.44
.3691	216.36	295.16	842.77
.4806	224.90	354.76	952.70
.6784	212.38	368.99	919.30
.8795	141.80	208.38	497.77

[a] calculated using fluctuation solution theory.
[b] Calculated using UNIQUAC, parameters from Nicolaides and Eckert (1978a).
The experimental data are from Nicolaides and Eckert (1978b)

b) The value of the excess enthalpy is of the order of experiment, but its dependence on temperature is wrong (Table 5-12).

The calculation of properties for the water-butanol system is a more severe test for any model, given the particular characteristic of water (hydrogen bonding, polarity, etc.). Table 5-13 shows the results for the water-butanol system. The agreement between experimental and calculated composition is not as good as aniline-cyclohexane, but it is not too bad. In the water-butanol system the binary parameters do not have a linear variation with temperature (Figure 5-7). Figure 5-8 shows the water activity at 353.16 K and at 393.16 K. The flatness of the curves at high water concentration explains the anomalous results of Table 5-13; a very small change in water activity produces a large change in the water mole fraction.

The extension of equation (5-1) to an n-component system is

$$\ln \gamma_i = \sum_{j=1}^{n} x_j \ln {}^j\gamma_i \qquad (5-8)$$

In equation (5-8) the ${}^j\gamma_i$ depends on binary parameters through equation (A-4). The multicomponent system brings a ${}^l k_{ij}$ parameter where $l \neq i \neq j$. From binary data we calculate ${}^i k_{ij}$ and ${}^j k_{ij}$, and ${}^l k_{ij}$ is obtained using

Table 5-13

Comparison of Liquid-Liquid Compositions for
Water (1)-Butanol (2)

T, K	x_1, phase'		x_1, phase"	
	Exp.	Calc.	Exp.	Calc.
313.15	.9831	.9847	.528	.514
323.15	.9835	.9839	.543	.538
333.15	.9833	.9833	.560	.560
343.15	.9827	.9827	.581	.581
353.15	.9823	.9402	.597	.606
363.15	.9796	.9397	.639	.623
373.15	.9760	.9391	.677	.640
383.15	.9720	.9806	.712	.646
388.15	.9660	---	.741	---
393.15	.9550	.9379	.778	.671

The experimental data are from Hill (1928).
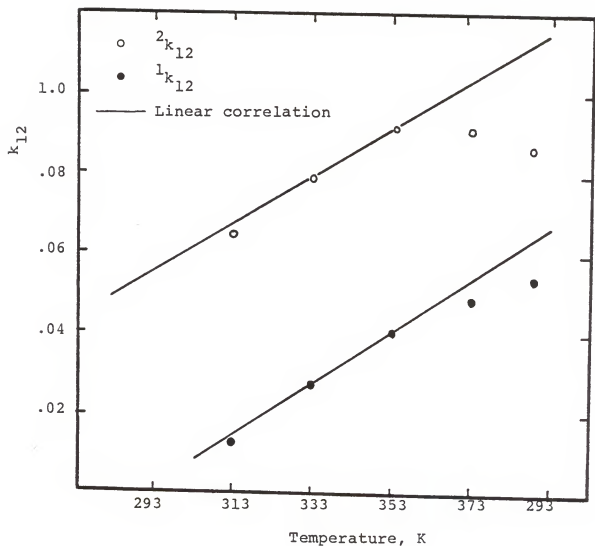The calculated data are from fluctuation solution
theory.

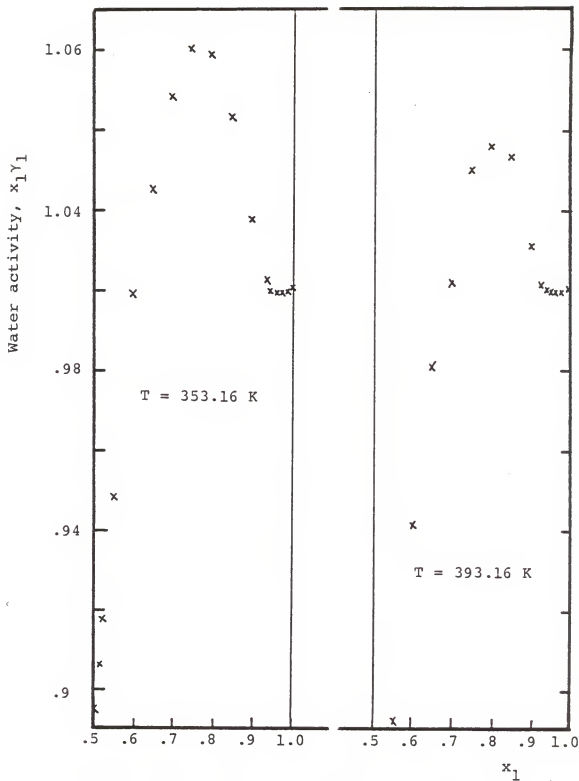Figure 5-7. Binary parameters in equation (5-1) for water (1) and butanol (2) at P = 1 atm.

Figure 5-8. Water (1) activity in butanol at P = 1 atm.

$$^1k_{ij} = \frac{1}{2} (^ik_{ij} + {}^ik_{ij}) \tag{5-9}$$

Table 5-14 and Figure 5-9 show the results of equilibrium calculations in n-heptane-cyclohexane-aniline system. The numbers at low concentration of cyclohexane are quite good, but, as noted in Table 5-14, in the mole heptane fraction range from 0.6 to 3.5 no solution was found. This occurs because, as Appendix C shows, the multifluid approach of equation (5-8) does not satisfy the Gibbs-Duhem equation.

Returning to the one-parameter, one-reference model, Table 5-15 and Figure 5-10 present the results of calculations on n-heptane-aniline-cyclohexane except that the pure component parameters T* and V* were adjusted so that the calculation is independent of the reference. The characteristic temperature of n-heptane was changed to fit the experimental n-heptane volume for the aniline reference. Also the characteristic temperature of cyclohexane was adjusted to fit the pure cyclohexane volume with the aniline reference. The characteristic temperature values are shown in Table 5-15. The numbers obtained with this new type of approach are not good, particularly on the aniline side, as shown in Figure 5-10 and Table 5-15.

The limited testing of the liquid-liquid calculations method using fluctuation solution theory shows some weaknesses in the perturbed hard-sphere models presented.

Table 5-14

Liquid-Liquid Equilibria in the System Heptane (1)-Cyclohexane (2)-Aniline (3)-Aniline (3) at T = 298.15 K

Experimental tie lines[a]

Phase'			Phase"		
x_1	x_2	x_3	x_1	x_2	x_3
.7059	.2104	.0837	.0559	.0166	.9274
.5558	.3504	.0938	.0502	.0453	.9045
.4395	.4576	.1029	.0454	.0684	.8862
.2272	.6487	.1241	.0312	.1390	.8298

Calculated tie lines[b]

Phase'			Phase"		
x_1	x_2	x_3	x_1	x_2	x_3
.7059	.2040	.0901	.0781	.0607	.8612
.5558	.3295	.1147	.082	.1056	.8124
.4395	.4243	.1362	.859	.1493	.7648
.0200	.8231	.1569	.0078	.2927	.6996
.0400	.7967	.1633	.0171	.3210	.6619
		NO SOLUTION WAS FOUND			
⋮					
.4000	.4561	.1439	.0886	.1692	.7423
.5000	.3752	.1248	.0836	.1249	.7914
.6000	.2930	.1070	.0808	.0916	.8276
.8000	.1230	.077	.0758	.0353	.8889
.9000	.0351	.0649	.0736	.0097	.9168

[a] Experimental data from Sørensen and Arlt (1980).
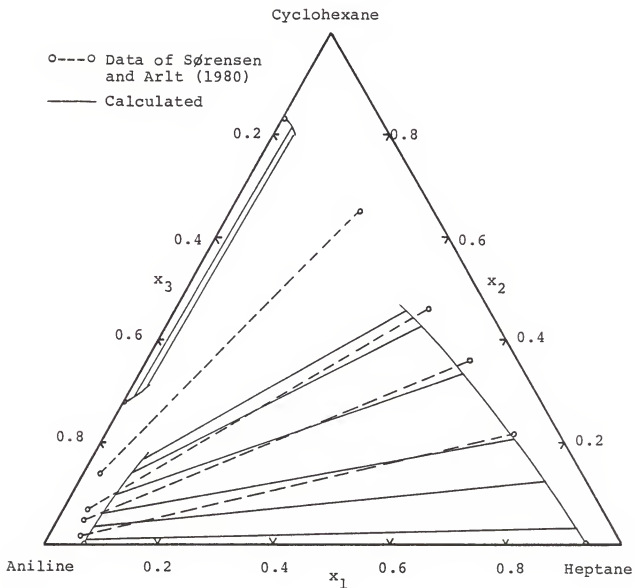[b] Calculated using scheme of Section 5.2 with equations (5-8) and (5-9).

Figure 5-9. Liquid-liquid equilibria in the system
heptane (1)-cyclohexane (2)-aniline (3)
at T = 298.15 K using multifluid references
and two parameters per binary

Table 5-15

Liquid-Liquid Equilibria in the System Heptane (1)-Cyclohexane (2)-Aniline (3) at T = 298.15 K

Experimental tie lines[a]

	Phase'			Phase"		
x_1	x_2	x_3		x_1	x_2	x_3
.7059	.2104	.0837		.0559	.0166	.9274
.5558	.3504	.0938		.0502	.0453	.9045
.4395	.4576	.1029		.0454	.0684	.8862
.2272	.6487	.1241		.0312	.1390	.8298

Calculated tie lines[b]

	Phase'			Phase"		
x_1	x_2	x_3		x_1	x_2	x_3
.8519	.0810	.0671		.0123	.0071	.9806
.6216	.2981	.0803		.0108	.0277	.9615
.3058	.5859	.1083		.0074	.0616	.9310
.0851	.7759	.1420		.0029	.0954	.9018

Characteristic Parameters

	Original	Modified
T_1^*	578.61	417.60
V_1^*	432.98	432.98
T_2^*	616.14	450.60
V_2^*	317.07	317.07
T_3^*	604.09	604.09
V_3^*	289.44	289.44

[a] Experimental data from Sørensen and Arlt (1980).
[b] Calculated using scheme of Section 5.2 with equation (A-4) that uses one binary parameter for each binary subsystem of the mixture.
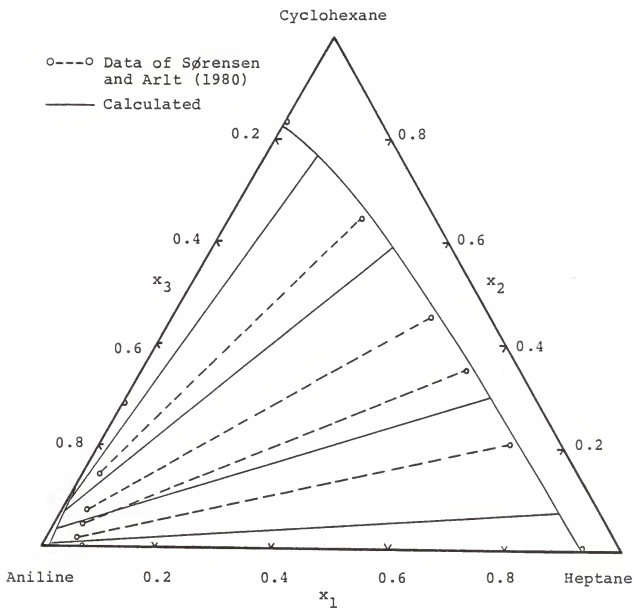
Figure 5-10. Liquid-liquid equilibria in the system heptane (1)-cyclohexane (2)-aniline (3) at T = 298.15 K using single fluid references and one parameter per binary.

In general for binary systems, the results are acceptable. Not only does the model, using the multifluid approach, correlate the phase envelope well, it provides multiproperty correlation with linear temperature parameters. On the other hand, the UNIQUAC model does not show these features. This comparison between models indicates a better temperature dependence built in the perturbed hard sphere model. We mentioned only the existence of closed-loop diagrams in binary systems. These mixtures have an upper and a lower critical solution temperature due to the balance of two opposite effects that have different temperature dependence. It is clear that the models presented in this chapter with linear dependent parameters cannot correlate the closed-loop system. We have made calculations using the multifluid approach that confirm this limitation. As a result, we cannot present modifications to the model to improve its temperature dependence.

In ternary systems, the results are not good. The multifluid approach violates the Gibbs-Duhem equation, and the mixing Gibbs energy surface generated by these activity coefficients does not possess, at some compositions, a common tangent plane in the regions corresponding to two different phases. The use of a one-parameter model is not good even for ternary systems with two inmiscible binaries which should be the easiest to correlate.

The results in ternary systems indicate that the composition dependence in the model is not quite right,

and this imperfection is a very important weakness. In the next chapter we make some suggestions to improve the composition dependence of direct correlation function integral models.

CHAPTER 6
MOLECULAR THERMODYNAMIC MODELS FOR DIRECT CORRELATION
FUNCTION INTEGRALS

6.1 Introduction

In applying fluctuation solution theory to liquid-
liquid equilibria, the methods used up to this point have
proven inadequate. The one-parameter model for binary sys-
tems in Section 5.2 is reasonably good, but it is not ade-
quate for ternary mixtures. Alternatives for overcoming
the one-parameter difficulty also had problems that led
to their rejection. Further, in Section 4.3 it is indi-
cated that the hard sphere mixture may not be a good
reference for describing direct correlation function
integrals.

An additional problem appears in the infinite dilution
behavior of the direct correlation function integrals. Even
in binary systems data show that the C_{ii}^{∞} depend on unlike
interactions between the components. The basic model, or
its modifications, do not take this into account, and
the only interaction that appears at infinite dilution is
that of hard spheres. One way to get rid of this limita-
tion is to include another term in the expansion, such as
quadratic in composition and density. Another way is to

look at different expressions that are obtained from models for classical excess Gibbs energy expressions.

Section 6.2 analyzes hard sphere mixtures as the reference. Section 6.3 presents the idea of including an extra term in the expansion. Section 6.4 examines the excess Gibbs energy models.

6.2 Behavior of Perturbed Hard Sphere

In Chapter 4 we concluded that for mixtures the particular choice of hard sphere equation for the reference term in equation (4-1) is not crucial. We now address the question of whether the hard sphere expression plus a linear density correction term is really a good way to model direct correlation function integrals.

In this section, we work with equations very similar to those of Chapter 4, except with different parameterizations. The characteristic temperature and characteristic volume were the basic parameters in Section 4.2. Here, they are replaced by the hard sphere diameters of the pure components. The direct correlation function integrals at constant temperature can be written

$$C_{ij}(\underline{x},\rho) = C_{ij}^{hs}(\underline{x},\rho,\sigma_1,\sigma_2) + \rho \, B_{ij} \qquad (6-1)$$

where $\underline{x}$ is the mole fractions vector, ρ is the density of the solution, σ_i is the hard sphere diameter of component

i, and B_{ij} is the coefficient of the correction term. In addition

$$B_{12} = B_{12} \ (1-\beta) \tag{6-2}$$

with β as a binary parameter used to match the calculated and the experimental activity coefficients.

The values of the hard sphere diameters are changed at constant density to make the B term a constant while simultaneously matching the experimental direct correlation function integrals.

Table 6-1 presents the results for the acetone (1)-carbon disulphide (2) system. The column under $-C_{ij}$ shows the values obtained using equation (6-1) with B_{ij} taken as the average of the difference between the experimental C_{ij} and the hard sphere C_{ij} (B_{ij}). At constant temperature the coefficients of the correction term and the hard sphere diameters are constant, so changing the density of the mixture should not change their values.

Table 6-2 presents the same kind of results as Table 6-1 but at a different mixture density. Unfortunately the average $\bar{B}_{ij}$ has increased around 10.0% rather than being the same as in Table 6-1.

Table 6-3 shows a comparison between C_{11} from different sources: experimental, calculated using equation (4-6) with characteristic parameters from Table 5-1, and $k_{12} =$ .04, calculated using equation (6-1) with $\beta = .0$ and

Table 6-1

Hard Sphere Analysis for Acetone (1)-Carbon Disulphide (2),
V = 58.67 cc/gr mol, T = 273.15 K

x_1	$-C_{11}^{hs}$	B_{11}	$-C_{12}^{hs}$	B_{12}	$-C_{22}^{hs}$	B_{22}
.00	130.38	4940.11	118.06	4459.46	106.90	4369.61
.25	150.72	4768.29	136.36	4581.17	123.37	4461.80
.50	175.54	4709.30	158.68	4584.54	143.43	4575.31
.75	206.14	4651.53	186.17	4580.06	168.13	4629.12
1.00	244.26	5225.00	220.40	4746.46	198.87	4522.73

$\bar{B}_{11} = 4864., \quad \bar{B}_{22} = 4511., \quad \bar{B}_{12} = 4580.$

x_1	$-C_{11}^{calc}$	$C_{11}^{exp}-C_{11}^{calc}$	$-C_{12}^{calc}$	$C_{12}^{exp}-C_{12}^{calc}$	$-C_{22}^{calc}$	$C_{22}^{exp}-C_{22}^{calc}$
.00	47.48	1.30	40.00	-2.05	30.02	-2.41
.25	67.82	-1.63	58.30	-0.83	46.48	-0.84
.50	92.64	-2.64	80.62	0.08	66.55	1.10
.75	123.24	-3.62	108.11	0.00	91.25	2.01
1.00	161.35	6.66	142.34	2.84	121.98	0.20

C_{ij}^{hs} and B_{ij} are those of equation (6-1).
$\bar{B}_{ij}$ is the average value of the B_{ij} values.
C_{ij}^{calc} is calculated using C_{ij}^{hs} and $\bar{B}_{ij}$.
C_{ij}^{exp} is the experimental C_{ij} reported in Chapter 3.

Table 6-2

Hard Sphere Analysis for Acetone (1)-Carbon Disulphide (2),
V = 57.44 cc/gr mol, T = 273.15 K

x_1	$-C_{11}^{hs}$	B_{11}	$-C_{12}^{hs}$	B_{12}	$-C_{22}^{hs}$	B_{22}
.00	148.68	5303.25	134.53	4832.73	121.73	4737.25
.25	173.30	5214.35	156.67	4972.90	141.64	4889.34
.50	203.68	5237.59	183.98	5115.02	166.18	5093.57
.75	241.59	5328.21	218.02	5245.56	196.74	5272.83
1.00	289.46	6295.82	260.98	5654.39	235.30	5309.67

$\bar{B}_{11} = 5476.,\ \bar{B}_{22} = 5060.,\ \bar{B}_{12} = 5164.$

	$-C_{11}^{calc}$	$C_{11}^{exp}-C_{11}^{calc}$	$-C_{12}^{calc}$	$C_{12}^{exp}-C_{12}^{calc}$	$-C_{22}^{calc}$	$C_{22}^{exp}-C_{22}^{calc}$
.00	64.00	7.65	54.80	4.40	43.20	3.94
.25	88.62	6.10	76.94	6.84	63.11	5.59
.50	119.00	6.50	104.24	9.31	87.64	10.41
.75	156.91	8.08	138.29	11.59	118.21	13.26
1.00	204.77	24.93	181.24	18.70	156.76	13.90

C_{ij}^{hs} and B_{ij} are those of equation (6-1).

$\bar{B}_{ij}$ is the average value of the B_{ij} values.

C_{ij}^{calc} is calculated using C_{ij}^{hs} and $\bar{B}_{ij}$.

C_{ij}^{exp} is the experimental C_{ij} reported in Chapter 3.

Table 6-3

Summary of C_{11} Calculated from Different Sources

V, cc/gmol	x_1	Experimental[a]	Characteristic Parameters[b]		Hard Sphere Diameter[c]		Modified B_{12}[d]	
58.67	.00	46.19	39.64	(- 6.55)[e]	47.48	(1.30)	37.27	(- 8.92)
	.25	69.45	57.56	(-11.8)	67.82	(-1.63)	55.57	(-13.88)
	.50	95.28	81.72	(-13.56)	92.64	(-2.64)	77.89	(-17.31)
	.75	126.86	114.61	(-12.25)	123.24	(-3.62)	105.38	(-21.48)
	1.00	154.69	160.70	(6.01)	161.35	(6.66)	139.60	(-15.09)
57.44	.00	56.35	47.65	(- 8.70)	64.00	(7.65)	52.00	(- 4.35)
	.25	82.52	68.80	(-13.70)	88.62	(6.10)	74.14	(- 8.38)
	.50	112.50	97.49	(-15.01)	119.00	(6.50)	101.45	(-11.05)
	.75	148.83	137.34	(-11.50)	156.91	(8.08)	135.50	(-13.33)
	1.00	179.85	194.25	(14.40)	204.78	(24.93)	178.45	(- 1.4)

[a]Sources of experimental data are quoted in Table 3-13.

[b]Calculated using equation (4-6) with characteristic parameters from Table 5-1 and $k_{12} = .04$.

[c]Calculated using equation (6-1) with $\beta = 0$.

[d]Calculated using equation (6-1) with $\beta = -.035$.

[e]Numbers in parentheses are difference with experiment.

calculated using equation (6-1) with $\beta = -.035$. The value of $\beta = -.035$ was obtained matching the experimental and the calculated activity coefficients. The number in parentheses in each column are the difference with experiment.

As pointed out before, the difference with experiment increases when C_{11} is calculated (using equation (6-1)) at a density different from that in which B_{11} was evaluated. We can make a similar observation for the C_{11} calculated with equation (4-6); the difference with experiment increases with increasing density. Another observation is that the C_{11} needed to match the activity coefficients are very different from the experimental C_{11}.

Figure 6-1 displays the mixture volume against mole fraction. The figure compares the experimental curve with results obtained using direct correlation function integrals calculated with equation (4-6) and calculated with equation (6-1). While the results using different references are somewhat different, the major feature is the obvious disagreement with experiment.

Table 6-4 presents results of the volumes and the activity coefficients using direct correlation function integrals calculated with equation (6-1) using B_{ij} as the average value of Table 6-1. Results with equation (4-6) for the C_{ij} are also included in the table. Small changes in the value of the coefficients of the linear density term produce large changes in the activity coefficient but
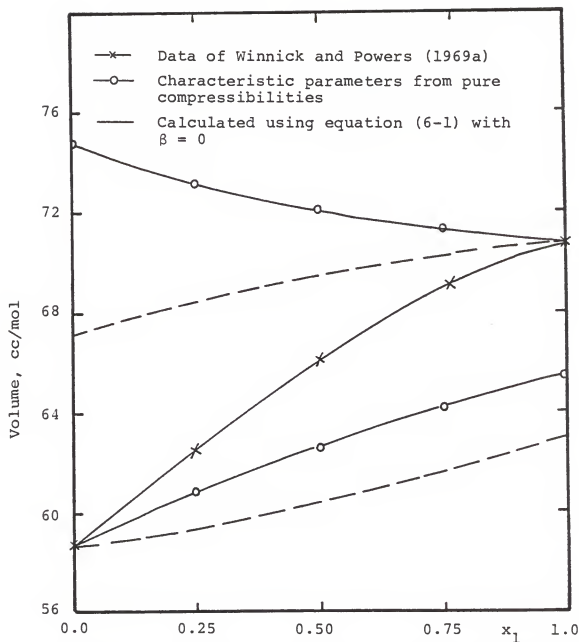
Figure 6-1. Mixture volume calculations for acetone (1)-carbon disulphide (2) at 273.15 K and 1 atm.

Table 6-4

Thermodynamic Properties Using Different Methods for Acetone (1) -Carbon Disulphide (2) at 273.15 K at 1 atm

a) Using binary parameter equal to zero.[a]

x_1	$^1 l_V$, cc/gr mol	$^1 l_V$, cc/gr mol	$^1\gamma_1$	$^2\gamma_1$	$^1\gamma_2$	$^2\gamma_2$
.00	67.61	58.87	.0429	.0254	1.0000	1.0000
.25	68.34	59.69	.1776	.1347	.8173	.7895
.50	69.23	60.63	.4738	.4221	.4545	.3989
.75	70.27	61.69	.8343	.8121	.1776	.1347
1.00	71.44	62.84	1.0000	1.0000	.0506	.0318

b) Using characteristic parameters.[b]

x_1	$^1 l_V$, cc/gr mol	$^1 l_V$, cc/gr mol	$^1\gamma_1$	$^2\gamma_1$	$^1\gamma_2$	$^2\gamma_2$
.00	74.79	58.87	8.3774	9.8993	1.0000	1.0000
.25	73.19	60.92	3.2280	3.3536	1.1457	1.1636
.50	72.09	62.62	1.6570	1.6612	1.7072	1.7678
.75	71.53	64.12	1.1291	1.1276	3.2260	3.3562
1.00	71.44	65.53	1.0000	1.0000	7.4670	7.6758

Table 6-4. Continued.

c) Using binary parameter equal to -.035.[c]

x_1	^1V, cc/gr mol	$^1Y_1$	$^2Y_1$	^1V, cc/gr mol	$^1Y_2$	$^2Y_2$
.00	67.61	4.9178	5.8945	58.87	1.0000	1.0000
.25	68.66	2.3852	2.6187	59.91	1.1079	1.1215
.50	69.64	1.4556	1.5117	60.92	1.4883	1.5571
.75	70.57	1.0956	1.1050	61.89	2.3853	2.6188
1.00	71.44	1.0000	1.0000	62.84	4.4978	5.2337

d) Using a modified B_{11}.[d]

x_1	^1V, cc/gr mol	$^1Y_1$	$^2Y_1$	^1V, cc/gr mol	$^1Y_2$	$^2Y_2$
.00	67.85	9.7074	12.8684	58.87	1.0000	1.0000
.25	68.88	3.4635	4.0075	59.90	1.1793	1.1793
.50	69.82	1.7719	1.8164	60.88	1.8919	1.8919
.75	70.67	1.1401	1.1555	61.80	4.0079	4.0079
1.00	71.44	1.0000	1.0000	62.68	10.9259	10.9259

[a] Calculated using equation (6-1) with $\beta = 0$.

[b] Calculated using equation (4-6) with characteristic parameters from Table 5-1 and $k_{12} = .04$.

[c] Calculated using equation (6-1) with $\beta = -.035$.

[d] Calculated using equation (6-1) with $\beta = -.035$ and $B_{11} = .99B_{11}^o$, where B_{11}^o is the B_{11} used in parts a and c.

The superscript indicates the reference used to do the calculations.

only a small change in the mixture volume. Changing B_{12} through the binary parameter produces no change in the calculation of the pure component volume and only a slight change at other concentrations. A change in B_{11} produces a small change at all concentrations. The changes in activity coefficient with a change in either B_{11} or B_{12} are very large. Table 6-5 compares the difference in the excess free Gibbs energy and in the activity coefficient of acetone calculated using acetone as the reference. The changes here are more significant; a change of 1.0% in B_{11} produces a change of 20.0% in the excess free Gibbs energy for an equimolar mixture and a change of more than 100.0% in the activity coefficient at infinite dilution. The changes produced by adjusting B_{12} to match the activity coefficient are even larger.

We can now say that the hard sphere reference is not generally a good concept. First, the coefficients of the correction term must be density dependent to correlate the data. Second, because of the difference in sign of C_{ij}^{hs} and the correction term, the calculated thermodynamic properties are very sensitive to values of these coefficients.

6.3 A Three Term Expansion for the Direct Correlation Function Integrals

In Chapter 3 we showed the experimental behavior of nonideal mixtures. We also found an expression for the

Table 6-5

Summary of Calculated Thermodynamic Properties

g^E/RT

x_1	Experimental	B_{12} from Matching C_{ij} [a]	B_{12} from Matching γ_s [b]	Modified B_{11} [c]
.00	.000	.000	.000	.000
.25	.304	-.583	.294	.420
.50	.545	-.768	.386	.552
.75	.311	-.568	.286	.410
1.00	.000	.000	.000	.000

$\ln \gamma_1$

x_1	Experimental	B_{12} from Matching C_{ij} [a]	B_{12} from Matching γ_s [b]	Modified B_{11} [c]
.00	8.28	0.04	4.92	9.71
.25	2.52	0.18	2.38	3.46
.50	1.47	0.47	1.45	1.71
.75	1.11	0.83	1.09	1.14
1.00	1.00	1.00	1.00	1.00

[a] Average value from Table 6-1, B_{12} = 4580.

[b] From equation (6-2) with β = -.035, B_{12} = 4740.3.

[c] A 1% decrease in the average value of Table 6-1, B_{11} = 4815.

The superscript indicates the reference used to do the calculations.

direct correlation function integrals as functions of the mixture compressibility, partial molar volume, and derivatives of the activity coefficients. The particular case of C_{11} for a binary 1-2 can be expressed as

$$(1-C_{11})^{\infty 1} = \frac{(\bar{v}_1^{\,2})^1}{v_2^{\,o} \kappa_2^{\,o} RT} + \left. \frac{d \ln \gamma_1}{dx_1} \right|_{T,P}^{\infty 1} \qquad (6\text{-}3)$$

where the superscript $\infty 1$ indicates that the mole fraction of component one goes to zero. From equation (6-1) we can get the infinite dilution expression for a perturbed hard sphere equation for C_{11}

$$(1-C_{11})^{\infty 1} = [(1-C_{11})^{hs}]^{\infty 1} + \rho_2^{\,o} B_{11} \qquad (6\text{-}4)$$

Comparing equation (6-3) with equation (6-4), we can point out an important weakness in the perturbation model. Equation (6-3) is highly dependent on 1-2 interaction, but in equation (6-4) the interaction 1-2 is only in the hard sphere mixture term. This makes explicit the inadequacy of the linear perturbation term.

Additional terms can be added to equation (6-1) to take account of this defect. These additional terms must have thermodynamic consistency

$$\frac{\partial}{\partial \rho_2} \left(\frac{\partial P}{\partial \rho_1} \right) = \frac{\partial}{\partial \rho_1} \left(\frac{\partial P}{\partial \rho_2} \right) \qquad (6\text{-}5)$$

where P stands for the pressure of the system. As

$$\frac{\partial P}{\partial \rho_1} = x_1(1-C_{11}) + x_2(1-C_{12}) \tag{6-6}$$

$$\frac{\partial P}{\partial \rho_2} = x_1(1-C_{12}) + x_2(1-C_{22}) \tag{6-7}$$

Replacing equation (6-6) and (6-7) in (6-5) we get

$$x_1 \ [\rho\frac{\partial}{\partial\rho_2} \ (1-C_{11}) - \rho \frac{\partial}{\partial\rho_1} \ (1-C_{12}) + C_{11} - C_{12}]$$

$$= x_2 \ [\rho \frac{\partial}{\partial\rho_1} \ (1-C_{22}) - \rho \frac{\partial}{\partial\rho_2} \ (1-C_{12}) + C_{22} - C_{12}]$$

$$\tag{6-8}$$

The only kind of extra term that satisfies equation (6-8)
is of the third virial type. The expression for one such
alternative is

$$C_{ij} \ (\underline{x},\underline{\rho}) = C_{ij}^{hs}(\underline{x},\rho,\sigma_1,\sigma_2) + \rho B_{ij}$$

$$+ \rho^2 \sum_{k=1}^{2} x_k \ D_{ijk} \tag{6-9}$$

The infinite dilution limit of equation (6-9) is for
$i = j = 1$

$$(1-C_{11})^{\infty 1} = [(1-C_{11})^{hs}]^{\infty 1} + \rho_2^{\ o} B_{11} + (\rho_2^{\ o})^2 D_{112} \tag{6-10}$$

where the term D_{112} contains information about the 1-2 interaction. Reordering equation (6-9) gives

$$C_{ij}(\underline{x},\rho) = C_{ij}^{hs} + \rho(B_{ij} + \rho \sum_{k=1}^{2} x_k D_{ijk})$$

$$= C_{ij}^{hs} + \rho B_{ij}' \qquad (6-11)$$

where B_{ij}' is the coefficient of the correction term that is linearly density dependent.

Unfortunately, the results of Table 6-3 and the plots in Chapter 4 (e.g., Figures 4-3, 4-5) indicate that the major error of the model is the reference (hs) fluid whose composition dependence is too strong, rather than too weak, particularly at compositions close to pure component. As a result, improvements in modelling must seek a fundamentally different concept from the rigid body reference idea.

6.4 Suggestion from Excess Gibbs Energy

We now examine classical expressions for activity coefficients in search of guidance in the modelling of direct correlation function integrals. We analyze a few semiempirical equations: Van Laar (Prausnitz, 1969), Solubility Parameter (Prausnitz, 1969), Wilson (Prausnitz, 1969), NRTL (Prausnitz, 1969), and UNIQUAC (Abrams and Prausnitz, 1975). We pay little attention to the physical

meaning of the parameters involved; our main interest is in the compositional form of the equations.

The activity coefficient expression from the Van Laar model is

$$\ln \gamma_1 = \frac{A}{[1 + \frac{A}{B} \frac{x_1}{x_2}]^2} \qquad (6\text{-}12a)$$

Taking the derivative of equation (6-12a) with respect to mole fraction of component 1 and introducing this result in equations (3-6) to (3-8) we get

$$(1-C_{11}) = \frac{\bar{v}_1^2}{v\kappa RT} - \frac{x_2^2 \, A'B'}{[x_2+B'x_1]^3} \qquad (6\text{-}13)$$

$$(1-C_{12}) = \frac{\bar{v}_1\bar{v}_2}{v\kappa RT} + \frac{x_1 x_2 \, A'B'}{[x_2+B'x_1]^3} \qquad (6\text{-}14)$$

$$(1-C_{22}) = \frac{\bar{v}_2}{v\kappa RT} - \frac{x_1^2 \, A'B'}{[x_2+B'x_1]^3} \qquad (6\text{-}15)$$

where $A' = 2A$ and $B' = 2B$

In solubility parameter theory, the activity coefficient has the following expression

$$\ln \gamma_1 = \frac{v_1^o \, x_2^2 \, v_2^{o^2} \, (\delta_1 - \delta_2)^2}{[x_1 \, v_1^o + x_2 \, v_2^o]} \qquad (6\text{-}16)$$

where v_i^o is the molar volume of component i and δ_i is the solubility parameter which is calculated using

$$\delta_i = \frac{\Delta U_1^V}{v_1^o}$$

with ΔU_1^V as the residual internal energy. Rearranging equation (6-16) and regrouping terms, we can recover equation (6-12a)

$$\ln \gamma_1 = \frac{A}{[1 + \frac{A}{B} \frac{x_1}{x_2}]^2} \tag{6-12b}$$

with $A = v_1^o (\delta_1 - \delta_2)$ and $B = v_1^o / v_2^o$

Because equation (6-12b) is a particular form of equation (6-12a), the direct correlation function integrals for the solubility parameter theory are given by equations (6-13) to (6-15). A similar result is obtained from the three suffix Margules equation. All of these are derived from the Wohl expansion (Prausnitz, 1969).

In the Wilson model, the activity coefficient expression is

$$\ln \gamma_1 = -\ln(x_1 + x_2 G_{12}) + x_2 [\frac{G_{12}}{x_1 + G_{12} x_2} - \frac{G_{21}}{G_{21} x_1 + x_2}] \tag{6-17}$$

Following the same procedure as for the Van Laar model, we get the equations for C_{11}, C_{12}, and C_{22}.

$$(1-C_{11}) = \frac{\overline{v}_1^2}{v\kappa RT} + \frac{x_2^2 A}{(x_1+x_2 B)^2} + \sum_{i=1}^{2} \frac{C_i x_2}{(x_1+x_2 D_i)^2} \qquad (6-18)$$

$$(1-C_{12}) = \frac{\overline{v}_1 \overline{v}_2}{v\kappa RT} - \frac{x_1 x_2 A}{(x_1+x_2 B)^2} + \sum_{i=1}^{2} \frac{C_i x_2}{(x_1+x_2 D_i)^2} \qquad (6-19)$$

$$(1-C_{22}) = \frac{\overline{v}_2^2}{v\kappa RT} + \frac{x_1^2 A}{(x_1+x_2 B)^2} + \sum_{i=1}^{2} \frac{C_i x_2}{(x_1+x_2 D_i)^2} \qquad (6-20)$$

where $A = (1-G_{12})^2$, $B = G_{12}$, $C_1 = -1$, $D_1 = B$, $C_2 = -1$, and $D_2 = 1/G_{21}$

The activity coefficient expression from the NRTL model is

$$\ln \gamma_1 = x_2^2 \left[\frac{\tau_{21} G_{21}^2}{(x_1+x_2 G_{21})^2} + \frac{\tau_{12} G_{12}}{(x_2+x_1 G_{12})^2} \right] \qquad (6-21)$$

Taking derivative with respect to mole fraction of component 1 and using equations (3-6) to (3-8)

$$(1-C_{11}) = \frac{\overline{v}_1^2}{v\kappa RT} + \sum_{i=1}^{2} \frac{A_i x_2^2}{(x_1+B_i x_2)^3} \qquad (6-22)$$

$$(1-C_{12}) = \frac{\overline{v}_1 \overline{v}_2}{v\kappa RT} - \sum_{i=1}^{2} \frac{A_i x_1 x_2}{(x_1+B_i x_2)^3} \qquad (6-23)$$

$$(1-C_{22}) = \frac{\overline{v}_2}{v\kappa RT} + \sum_{i=1}^{2} \frac{A_i \, x_1^2}{(x_1+B_i x_2)^3} \qquad (6-24)$$

where $A_1 = \tau_{21}G_{21}^2$, $B_1 = G_{21}$, $A_2 = \tau_{12} G_{12}^2$, and $B_2 = G_{12}$

In the UNIQUAC model, the activity coefficient equation is

$$\ln \gamma_1 = \ln \frac{\phi_1}{x_1} + (\frac{z}{2}) \, q_1 \, \ln \frac{\theta_1}{\phi_1} + \phi_2 \, (\ell_1 - \frac{r_1}{r_2} \ell_2)$$

$$- q_1' \, \ln \, (\theta_1' + \theta_1' \, \tau_{21})$$

$$+ \theta_1' \, q_1' \, [\frac{\tau_{21}}{\theta_1'+\theta_2' 21} - \frac{\tau_{12}}{\theta_2'+\theta_1'\tau_{12}}] \qquad (6-25)$$

The direct correlation function integrals that we get from equation (6-25) are

$$(1-C_{11}) = \frac{\overline{v}_1^2}{v\kappa RT} + \sum_{i=1}^{4} \frac{x_2 A_i}{(x_1+B_i x_2)} + \sum_{j=1}^{2} x_2 \frac{A_j}{(x_1+B_j x_2)^2}$$

$$+ x_2^2 \frac{C}{(x_1+Dx_2)^2} \qquad (6-26)$$

$$(1-C_{12}) = \frac{\overline{v}_1 \overline{v}_2}{v\kappa RT} - \sum_{i=1}^{4} \frac{x_1 A_i}{(x_1+B_i x_2)} - \sum_{j=1}^{2} x_1 \frac{A_j}{(x_1+B_j x_2)^2}$$

$$+ x_1 x_2 \frac{C}{(x_1+Dx_2)^2} \qquad (6-27)$$

$$(1-C_{22}) = \frac{\overline{V}_2^2}{V \kappa RT} - \sum_{i=1}^{4} x_1 \frac{A_i'}{(x_1+B_i'x_2)} - \sum_{j=1}^{2} x_2 \frac{A_j'}{(x_1+B_j'x_2)^2}$$

$$+ x_1^2 \frac{C}{(x_1+Dx_2)^2} \qquad (6-28)$$

where the parameters of equations (6-26) to (6-28) are a complex combination of the parameters of equation (6-25).

The Wilson, NRTL, and UNIQUAC are local composition models. These models describe excess properties only. For representing the thermodynamic properties of mixtures at high pressure, it is convenient to use an equation of state in all the ranges of densities. With the equation of state approach the election of references is avoided, and mixtures containing supercritical components can be described without the use of hypothetical reference state. The idea of incorporating the local composition concept into an equation of state has recently been the subject of study (Whiting and Prausnitz, 1982; Mollerup, 1981).

An equation for the excess Gibbs energy from such equations of state is

$$g^E = (-RT/\alpha) \sum_{i=1}^{2} x_i \ln \sum_{j=1}^{2} x_j \exp \left[\alpha(a_{ji}-a_{ii})/bRT\right]$$

$$(6-29)$$

Whiting and Prausnitz (1982) developed equation (6-29) as an example of the procedure of including the local composition

concept into an equation of state. The applicability of equation (6-29) is very limited because it was assumed that the molecules of the mixtures were of approximately the same size.

Using the second derivative of equation (6-29) with respect to component 1 in equations (3-6) to (3-8)

$$(1-C_{11}) = \frac{\overline{V}_1^2}{V\kappa RT} + \frac{x_2^2 A}{(x_1+x_2 B)^2} + \sum_{i=1}^{2} \frac{C_i x_2}{(x_1+x_2 D_i)^2} \qquad (6-30)$$

$$(1-C_{12}) = \frac{\overline{V}_1 \overline{V}_2}{V\kappa RT} - \frac{x_1 x_2 A}{(x_1+x_2 B)^2} - \sum_{i=1}^{2} \frac{C_i x_i}{(x_1+x_2 D_i)^2} \qquad (6-31)$$

$$(1-C_{22}) = \frac{\overline{V}_2^2}{V\kappa RT} + \frac{x_1^2 A}{(x_1+x_2 B)^2} + \sum_{i=1}^{2} \frac{C_i x_2}{(x_1+x_2 D_i)^2} \qquad (6-32)$$

with $A = (1 - \exp [\alpha(a_{21}-a_{11})/bRT])^2/\alpha$, $B = (\exp [\alpha(a_{21}-a_{11})/bRT])/\alpha$, $C_1 = -1/\alpha$, $D_1 = B$, $C_2 = C_1$, and $D_2 = (\exp [\alpha(a_{11}-a_{12})/bRT])/\alpha$

It is evident that equations (6-30) to (6-32) are identical to equations (6-18) to (6-20). Then, the form of the direct correlation function integrals for this particular local-composition equation of state is the same as those for the Wilson model.

We do not pursue further in the search of forms with different and more complex equations of state because we assume they may produce direct correlation function integrals similar to those from Wilson, NRTL, and UNIQUAC.

It is well known that the Wohl form and the Wilson form represent extremes of compositional behavior of $\ln \gamma_i$. The former shows liquid-liquid behavior with relatively small values of $\ln \gamma_i^{\infty}$, whereas the Wilson equation cannot yield immiscibility. The other local composition models are in between.

Comparison of the appropriate equations in (6-13) to (6-32) show that the trend for C_{ii} is from a variation like

$$\frac{A_{ij} \, x_j^2}{(1+B_{ij}x_j)^3}$$

to terms of the form

$$\frac{A_{ijn} \, x_j^n}{(1+B_{ijn}x_j)^2}$$

where $j \neq i$ and $n = 1,2$. Clearly these all include binary parameters for C_{ii}^{∞} $(x_j \to 1)$. The major change in the representation is to include a less strong (quadratic rather than cubic), but more flexible (more terms) variation of C_{ii} with x_j.

Using these ideas, we can suggest an alternative approach in modelling C_{ij}. As it is very convenient to model small numbers and the term that contains the partial molar volume and the isothermal compressibility is numerically the most important, we suggest to model the difference $(1-C_{ij}) - (1-C_{ij})^{id}$. The properties present in $(1-C_{ij})^{id}$

are pure component properties that make the computation of the ideal direct correlation function integrals easy. For modelling this difference we suggest the following form

$$\Delta C_{11} = (1-C_{11}) - \frac{1}{\rho_1^O \, \kappa_1^O \, RT} = \frac{A_{12} x_2 \, (1+C_{12} x_2)}{(x_1 + B_{12} x_2)^2} \qquad (6-33)$$

The equations for ΔC_{12} and ΔC_{22} are similar to equation $(6-33)$.

Finally, we must point out two serious weaknesses of this suggestion. First, it lacks a theoretical basis. The parameters have no physical meaning, and they need to be evaluated from binary experimental data. Second, the extension to multicomponent systems is highly uncertain. On the other hand, the main advantage is that the calculated properties are not very sensitive to the particular form of the direct correlation function integrals and the results can be accurate.

CHAPTER 7
CONCLUSIONS

In this work we have used a unique approach to calculate liquid-phase thermodynamic properties. The fluctuation solution theory, as we call it, derived from rigorous statistical mechanical relations, expresses derivative properties as functions of direct correlation function integrals.

The thermodynamic properties of interest (activity coefficients and pressure) are obtained by integrating these relations. Other approaches get the same properties by differentiation of excess Gibbs energy models or P-v-T-x equations of state.

The most important assumption made in fluctuation solution theory calculations is that the direct correlation function integrals may be modeled with equations of simple form. The foundation of such assumption is that it has been found that for dense fluids these integrals are apparently insensitive to the details of the intermolecular interactions (Gubbins and O'Connell, 1974).

The Mathias Van der Waals model (1978) has been extended for use in describing the solubility of gases in binary solvents and solubility of liquids in liquids. We have made modifications in the model to improve the

modelling of liquid-liquid equilibria. In the process we have made an extensive determination of direct correlation function integrals from experimental data to find out how these integrals really do vary with composition. Finally, we have made some suggestions to improve the model for further work.

In spite of the relative lack of success in describing the liquid-liquid equilibria, the approach has considerable potential. The assumption of simplicity still is valid, and it is clear that the direct correlation function integrals are insensitive to the details of the intermolecular forces. Whatever complexity appears with some of the experimental direct correlation function integrals is probably due to uncertainty in the correlating experimental data.

The results of Chapter 4 that extend early calculations of Mathias prove that the model is excellent in describing gas-liquid equilibria. Unfortunately, the application of the model in liquid-liquid calculations shows some weaknesses. For example, the perturbed hard-sphere model does not have precisely the right temperature dependence. Thus, closed-loop systems cannot be correlated even with parameters linearly dependent on temperature.

Results for ternary systems indicate that the composition dependence in the model is inadequate. The main difficulty seems to be that the model uses only one binary parameter whereas more are necessary.

Further, at infinite dilution in binary systems, data show that the DCFI strongly depend on interactions between the components, but the model has no term to account for these interactions.

A suggestion is made to overcome the infinite dilution problem. It may also apply to multicomponent liquid-liquid equilibria.

The general concept is to incorporate an additional term in the expansion of the perturbed hard-sphere model. The term is quadratic in composition and resembles the third term of the virial equation of state. With this modification the interaction between components at infinite dilution is incorporated into the model, and the necessary binary parameters are available to describe liquid-liquid equilibria.

Another suggestion for modelling direct correlation function integrals is to use the general forms obtained from excess Gibbs energies. In such an expression, the parameters have no physical meaning and they need to be evaluated from experimental data. As a result, this is less satisfying than the above idea.

It is hoped that the present investigation will have provided a basis for analysis of data and establishment of models of liquid solutions that will lead to more accurate correlations and predictions of these most complex systems.

APPENDIX A
EQUATIONS IN THE BASIC MODEL

Introducing (4-6) in the equations of Chapter 2, we obtain the thermodynamic properties for a multicomponent fluid phase.

The pressure equation is

$$\frac{p^f - p^r}{RT} = p^{hs}(T, \underline{\rho}^f) - p^{hs}(T, \underline{\rho}^r)$$

$$+ \sum_{i=1}^{n} \sum_{j=1}^{n} [\rho_i^f \rho_j^f - \rho_i^r \rho_j^r] \, v_{ij}^* \, (g_{ij} - f_{ij}) \quad \text{(A-1)}$$

where the hard sphere term is the Carnahan-Starling (1969) equation for a hard sphere mixture

$$\frac{p^{hs}}{RT}(T, \underline{\rho}) = \frac{6}{\Pi} \left[\frac{\xi_o}{(1-\xi_3)} + \frac{3\xi_1\xi_2}{(1-\xi_3)^3} + \frac{\xi^3(3-\xi_3)}{(1-\xi_3)^3} \right] \quad \text{(A-2)}$$

where

$$\xi_k = \frac{\Pi}{6} \sum_{i=1}^{n} \rho_i \sigma_i^k \qquad k = 0,1,2,3 \quad \text{(A-3)}$$

and where f_{ij}, g_{ij} are defined in (4-9a), (4-9b), (4-9c).

The activity coefficients have the following expression

$$\ln \frac{\gamma_i^f}{\gamma_i^r} = \frac{\mu_i^{hs}(T, \underline{\rho}^f)}{RT} - \frac{\mu_i^{hs}(T, \underline{\rho}^r)}{RT}$$

$$+ 2 \sum_{j=1}^{n} [\rho_j^f - \rho_j^r] v_{ij}^* (g_{ij} - f_{ij}) \qquad (A-4)$$

where the hard sphere chemical potential is given by the Carnahan-Starling expression

$$\frac{\mu_i^{hs}}{RT}(T, \underline{\rho}) = \ln \rho - \ln (1 - \xi_3)[1 - (\frac{\xi_2 \sigma_i}{\xi_3})^2 [3 - 2 (\frac{\xi_2 \sigma_i}{\xi_3})]]$$

$$+ [3(\xi_2 \sigma_i + \xi_1 \sigma_i^2) - (\xi_2 \sigma_i)^3 (2 - \xi_3)/\xi_3^2]/(1 - \xi_3)$$

$$+ \frac{3}{\xi_3} (\frac{\xi_2 \sigma_i}{1 - \xi_3})^2 + \frac{\pi}{6} \sigma_i^3 \frac{P^{hs}(T, \underline{\rho})}{RT} \qquad (A-5)$$

The cross characteristic parameters, v_{ij}^* and T_{ij}^* are defined by

$$v_{ij}^* = \frac{(v_{ii}^{*1/3} + v_{jj}^{*1/3})^3}{8} \qquad (A-6)$$

$$T_{ij}^* = (1 - k_{ij}) (T_i^* - T_j^*)^{1/2} \qquad (A-7)$$

and the function f and g are given by the following expression

$$f = \frac{0.65386227}{(T/T_i^*)^{0.16067976}} \qquad\qquad T/T_i^* \geq 0.73 \qquad (A-8)$$

$$= 0.807662393 \exp\left[-0.22010926\,(T/T_i^*)\right]$$

$$T/T_i^* \leq 0.73 \qquad (A-9)$$

$$g = 0.3625065 - \frac{0.7140666}{T}\,T_{ij}^* - \frac{1.7543882}{T^2}\,T_{ij}^{*\,2}$$

$$+ \frac{0.470750}{T^3}\,T_{ij}^{*\,3} - \frac{0.0041793}{T^8}\,T_{ij}^{*\,8} \qquad (A-10)$$

The relation between σ_i and f_i that is needed to obtain the hard sphere diameter from f is

$$\frac{2\Pi}{3}\,\frac{\sigma_i^{\,3}}{v_{ii}^*} = f_i \qquad\qquad\qquad (A-11)$$

APPENDIX B
HARD SPHERE EQUATIONS FOR MIXTURES

The Carnahan-Starling (1969) equation was used by
Mathias (1978) in modelling direct correlation function
integrals. However, introducing a parameter, α, it is
possible to generate other equations for hard sphere
fluids. The pressure equation is

$$p^{hs} = \frac{6kT}{\Pi} \left(\frac{\xi_0}{(1-\xi_3)} + 3 \frac{\xi_1 \xi_2}{(1-\xi_3)^2} + 3 \frac{\xi_2^3}{(1-\xi_3)^3} \right.$$
$$\left. + \alpha \frac{\xi_3 \xi_2^3}{(1-\xi_3)^3} \right) \tag{B-1}$$

where

$$\xi_k = \frac{1}{6} \Pi \sum_{i=1}^{n} \rho_i \sigma_i^k \qquad k = 0,1,2,3 \tag{B-2}$$

k is the Boltzmann constant, ρ_i the number density, and
σ_i the hard sphere diameter of component i. In the follow-
ing equations, the superscript hs will be dropped, but all
the thermodynamic properties will be for hard spheres.

The pressure and chemical potential are related
through the Helmholtz free energy by thermodynamic relations

$$P = -\left.\frac{\partial A}{\partial V}\right|_{T,\underline{N}} \tag{B-3}$$

$$\mu_i = -\left.\frac{\partial A}{\partial N_i}\right|_{T,N_{j\neq i}} \tag{B-4}$$

We obtain the Helmholtz free energy by integration of equation (B-3), and then we use equation (B-4) to get an expression for the chemical potential of a hard sphere mixture.

$$\frac{\mu_i}{kT} = \frac{\ln \rho_i \Lambda_i^3}{q_{int,i}} + \frac{\Pi P \sigma_i^3}{6kT} - \ln(1-\xi_3)$$

$$+ \frac{3 \xi_2 \sigma_i}{(1-\xi_3)} + \frac{3 \xi_1 \sigma_i^2}{(1-\xi_3)} + \frac{9 \xi_2^2 \sigma_i^2}{2(1-\xi_3)^2}$$

$$- 3\alpha \left(\frac{\xi_2^2 \sigma_i}{\xi_3}\right)^2 \left[\ln(1-\xi_3) + \frac{\xi_3}{(1-\xi_3)} - \frac{\xi_3^2}{2(1-\xi_3)^2}\right]$$

$$+ \alpha \left(\frac{\xi_2 \sigma_i}{\xi_3}\right)^2 \left[2 \ln(1-\xi_3) + \xi_3 \frac{(2-\xi_3)}{(1-\xi_3)}\right] \tag{B-5}$$

where Λ_i is the thermal De Broglie wavelength, and $q_{int,i}$ is the molecular internal partition function.

The relation between the direct correlation function integrals is given by equation (2-23)

$$\left.\frac{\partial \mu_i/kT}{\partial \rho_j}\right|_{T,\rho_{k\neq j}} = \frac{\delta_{ij}}{\rho_i} - \frac{C_{ij}}{\rho} \tag{2-23}$$

Using equations (2-23) and (B-5) we get the i-j direct
correlation function integral for a multicomponent hard
sphere mixture.

$$
-C_{ij}^{hs} = \rho \left\{ \frac{1}{(1-\xi_3)} \, 1/6\Pi\sigma_j^{\,3} + \frac{3\Pi}{6} \frac{\sigma_j^{\,2}\sigma_i}{(1-\xi_3)} \right.
$$

$$
+ \frac{3\Pi}{6} \frac{\sigma_j^{\,3}\xi_2\sigma_i}{(1-\xi_3)^2} + \frac{3\Pi}{6} \frac{\sigma_j\sigma_i^{\,2}}{(1-\xi_3)} + \frac{3\Pi}{6} \frac{\sigma_j^{\,3}\xi_1\sigma_i^{\,2}}{(1-\xi_3)^2}
$$

$$
+ 9\xi_2 \frac{\Pi}{6} \frac{\sigma_j^{\,2}\sigma_i^{\,2}}{(1-\xi_3)^2} + 9 \frac{\Pi}{6} \frac{\sigma_j^{\,3}\xi_2^{\,2}\sigma_i^{\,2}}{(1-\xi_3)^3}
$$

$$
- 3\alpha \frac{2\xi_2\sigma_i}{\xi_3} \left(\frac{\Pi}{6} \frac{\sigma_j^{\,2}\sigma_i}{\xi_3} - \frac{\Pi}{6} \frac{\sigma_j^{\,3}\xi_2\sigma_i}{\xi_3^{\,2}} \right)
$$

$$
\left[\ln(1-\xi_3) + \frac{\xi_3}{(1-\xi_3)} - \frac{\xi_3^{\,2}}{2(1-\xi_3)^2} \right]
$$

$$
+ 3\alpha(\xi_2\sigma_i)^2 \frac{\Pi}{6} \frac{\sigma_j^{\,3}}{(1-\xi_3)^3}
$$

$$
- \alpha \, 3 \left(\frac{\xi_2\sigma_i}{\xi_3} \right)^2 \left[\frac{\Pi}{6} \frac{\sigma_j^{\,3}\xi_2\sigma_i}{\xi_3^{\,2}} - \frac{\Pi}{6} \frac{\sigma_j^{\,2}\sigma_i}{\xi_3} \right]
$$

$$
\left(2 \ln (1-\xi_3) + \xi_3 \frac{(2-\xi_3)}{(1-\xi_3)} \right)
$$

$$
+ \alpha \left(\frac{\xi_2\sigma_i}{\xi_3} \right)^3 \left[\Pi/6 \; \sigma_j^{\,3}\xi_3 \frac{(2-\xi_3)}{(1-\xi_3)^2} - 2\Pi/6 \frac{\sigma_j^{\,3}\xi_3}{(1-\xi_3)} \right]
$$

$$+ \sigma_i{}^3/\frac{\Pi}{6} \ (1-\xi_3) \ + \ \frac{\xi_0 \Pi \sigma_j{}^3 \sigma_i{}^3}{6(1-\xi_3)^2} \ + \ 3\Pi/6 \ \frac{\sigma_j \sigma_i{}^3 \xi_2}{(1-\xi_3)^2}$$

$$+ \ 3\Pi/6 \ \frac{\sigma_j{}^2 \sigma_i{}^3 \xi_1}{(1-\xi_3)^2} \ + \ 6\Pi/6 \ \frac{\sigma_j{}^3 \xi_1 \xi_2 \sigma_i{}^3}{(1-\xi_3)^2}$$

$$+ \ 9\Pi/6 \ \frac{\xi_2{}^2 \sigma_j{}^2 \sigma_i{}^3}{(1-\xi_3)^3} \ + \ 9\Pi/6 \ \frac{\sigma_j{}^3 \xi_2{}^3 \sigma_i{}^3}{(1-\xi_3)^4}$$

$$+ \ \alpha[\ \Pi/6 \ \frac{\sigma_i{}^3 \sigma_j \xi_2{}^3}{(1-\xi_3)^3} \ + \ 3\Pi/6 \ \frac{\sigma_i{}^3 \sigma_j{}^3 \xi_3 \xi_2{}^2}{(1-\xi_3)^3}$$

$$+ \ 3\Pi/6 \ \frac{\sigma_j{}^3 \sigma_i{}^3 \xi_3 \xi_2{}^3}{(1-\xi_3)^4} \ ]\} \tag{B-6}$$

For a pure component system equation (B-1) reduces to

$$P = kT\rho \ \frac{(1 + \eta + \eta^2 + \alpha\eta^3)}{(1-\eta)^3} \tag{B-7}$$

where η, the packing fraction, is ξ_3. Equation (B-7) is equation (4-14) in Section 4.3.

In equation (B-7) when α is equal to -1, the Carnahan-Starling equation is recovered, when $\alpha = 0$ the Percus-Yevick compressibility equation is recovered, and when $\alpha = -3$ the Percus-Yevick virial equation is recovered.

The direct correlation function integral for a pure component is

$$C = \frac{-8\eta + 2\eta^2 - 4(1+\alpha) \ \eta^3 + (1+\alpha) \ \eta^4}{(1-\eta)^4} \tag{B-8}$$

In the particular case of Carnahan-Starling, equation (B-8) becomes

$$C = \frac{2\eta(\eta-4)}{(1-\eta)^4} \qquad\qquad (B-9)$$

APPENDIX C

GIBBS-DUHEM ANALYSIS OF THE MULTIFLUID APPROACH

The starting point in the multifluid approach is equation (5-1)

$$\ln \gamma_i = \sum_{j=1}^{n} x_j \ln {}^j\gamma_i \qquad (C-1)$$

where ${}^j\gamma_i$ is the activity coefficient of component i using reference j, taking derivatives on both sides of equation (C-1) at constant T and ρ

$$d \ln \gamma_i = \sum_{j=1}^{n} x_j \, d \ln {}^j\gamma_i + \sum_{j=1}^{n} d \, x_j \ln {}^j\gamma_i \qquad (C-2)$$

If the Gibbs-Duhem equation is applied to the activity coefficients defined by equation (C-1), we can write using equation (C-2)

$$\sum_{i=1}^{n} x_i \, d \ln \gamma_i = 0$$

$$= \sum_{i=1}^{n} x_i \sum_{j=1}^{n} x_j \, d \ln {}^j\gamma_i$$

$$+ \sum_{i=1}^{n} x_i \sum_{j=1}^{n} d \, x_j \ln {}^j\gamma_i \qquad (C-3)$$

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As

$$\sum_{i=1}^{n} x_i \sum_{j=1}^{n} x_j \, d \ln {}^{j}\gamma_i = \sum_{j=1}^{n} x_j \sum_{i=1}^{n} x_i \, d \ln {}^{j}\gamma_i$$

$$= 0 \qquad\qquad (C-4)$$

because

$$\sum_{i=1}^{n} x_i \, d \ln {}^{j}\gamma_i = 0 \qquad\qquad (C-5)$$

by model construction, then for equation (C-3) to be true

$$\sum_{i=1}^{n} x_i \sum_{j=1}^{n} d \, x_j \ln {}^{j}\gamma_i = 0 \qquad\qquad (C-6)$$

as the mole fractions are not independent, equation (C-6) can be rearranged

$$\sum_{i=1}^{n} x_i \sum_{j \neq k} d \, x_j \, (\ln {}^{j}\gamma_i - \ln {}^{k}\gamma_i)$$

$$= \sum_{j \neq k} d \, x_j \, (\sum_{i=1}^{n} x_i \, (\ln {}^{j}\gamma_i - \ln {}^{k}\gamma_i)$$

$$= 0 \qquad\qquad (C-7)$$

In equation (C-7) the mole fraction differentials (d x_j; j≠k) are independent, then

$$\sum_{i=1}^{n} x_i \, (\ln \, {}^{j}\gamma_i - \ln \, {}^{k}\gamma_i) = 0 \quad \text{for all } j \neq k \qquad (C\text{-}8)$$

Forming a linear combination of (C-8) equations

$$\sum_{j \neq k} x_j \sum_{i=1}^{n} x_i \, (\ln \, {}^{j}\gamma_i - \ln \, {}^{k}\gamma_i) = 0$$

or

$$\sum_{j=1}^{n} x_j \sum_{i=1}^{n} x_i \, \ln \, {}^{j}\gamma_i = \sum_{i=1}^{n} x_i \, \ln \, {}^{k}\gamma_i \qquad (C\text{-}9)$$

or

$$\ln \, {}^{k}\gamma_i = \sum_{j=1}^{n} x_j \, \ln \, {}^{j}\gamma_i \quad \text{for any } k \qquad (C\text{-}10)$$

Equation (C-10) says that the only possible choice of reference that will satisfy the Gibbs-Duhem equation is a pure component reference.

We can extract the same conclusion by starting with the definition of excess free Gibbs energy in the multi-fluid approach

$$\frac{g^E}{RT} = \sum_{i=1}^{n} x_i \, \ln \, \gamma_i$$

$$= \sum_{i=1}^{n} x_i \sum_{j=1}^{n} x_j \, \ln \, {}^{j}\gamma_i \qquad (C\text{-}11)$$

By definition of the activity coefficient (which assumes the Gibbs-Duhem equation)

$$\ln \gamma_k = \frac{\partial}{\partial N_k} \left(\frac{N g^E}{RT} \right) \Bigg|_{P,T,N_{1 \neq k}} \tag{C-12}$$

where N_i are the number of moles of component i and N the total number of moles, using equation (C-11) in equation (C-12)

$$\frac{\partial}{\partial N_k} \left(\frac{N g^E}{RT} \right) \Bigg|_{P,T,N_{1 \neq k}}$$

$$= \frac{\partial}{\partial N_k} \left[\frac{1}{N} \sum_{i=1}^{n} N_i \sum_{j=1}^{n} N_j \ln {}^j\gamma_i \right] \Bigg|_{P,T,N_{1 \neq k}}$$

$$= - \frac{1}{N^2} \sum_{i=1}^{n} N_i \sum_{j=1}^{n} N_j \ln {}^j\gamma_i + \frac{1}{N} \sum_{j=1}^{n} N_j \ln {}^j\gamma_k$$

$$+ \frac{1}{N} \sum_{i=1}^{n} N_i \ln {}^k\gamma_i$$

$$+ \frac{1}{N} \sum_{i=1}^{n} N_i \sum_{j=1}^{h} N_j \frac{\partial \ln {}^j\gamma_i}{\partial N_k} \Bigg|_{P,T,N_{1 \neq k}} \tag{C-13}$$

As

$$\frac{1}{N} \sum_{i=1}^{n} N_i \sum_{j=1}^{n} N_j \frac{\partial \ln {}^j\gamma_i}{\partial N_k}$$

$$= \frac{1}{N} \sum_{j=1}^{n} N_j \sum_{i} N_i \frac{\partial \ln {}^j\gamma_i}{\partial N_i} = 0 \tag{C-14}$$

Equation (C-13) reduces to

$$\ln \gamma_k = \sum_{j=1}^{n} x_j \ln {}^j\gamma_k + \sum_{i=1}^{n} x_i [\ln {}^k\gamma_i - (\sum_{j=1}^{n} x_j \ln {}^j\gamma_i)]$$

$$(C-15)$$

but

$$\sum_{j=1}^{n} x_j \ln {}^j\gamma_k = \ln \gamma_k$$

Then, we can write equation (C-15) as

$$\ln \gamma_k = \ln \gamma_k + \sum_{i=1}^{n} x_i [\ln {}^k\gamma_i - (\sum_{j=1}^{n} x_j \ln {}^j\gamma_i)] \quad (C-16)$$

Equation (C-16) can be true if

$$\sum_{i=1}^{n} x_i [\ln {}^k\gamma_i - (\sum_{j=1}^{n} x_j \ln {}^j\gamma_i)] = 0 \quad (C-17)$$

or

$$\ln {}^k\gamma_i = \sum_{j=1}^{n} x_j \ln {}^j\gamma_i \quad \text{for any k} \quad (C-18)$$

Equation (C-18) is the same as equation (C-10).

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.
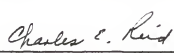
John P. O'Connell, Chairman
Professor of Chemical Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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